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# PRINCIPLES OF CHEMISTRY.

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# PRINCIPLES

OF

# CHEMISTRY,

FOUNDED ON

# MODERN THEORIES.

LEEDS SCHOOL OF MEDICINE

BY

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LEEDS SCHOOL OF MEDICINE

# TRANSLATOR'S PREFACE.

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M. NAQUET's work on Chemistry is one which, while setting forth the modern theories of the science, gives as much of the practical results obtained by analysis and experiment, and of the mode of preparation and the properties of the elements and their compounds, as is necessary for the student without being too bulky for its contents to be easily mastered, that portion which treats of Organic Chemistry being especially valuable. M. Naquet explains and gives with great ability the arguments for and against his theories and those of other chemists, thus affording the facts and reasoning on which they are based, and the means of judging of their respective values, while many of the views set forth, and of the experiments given, are of interest from their comparative novelty. Such a work seemed to me to be needed in the English language, and I therefore undertook its translation.

M. Kékulé's diagrams are, I think, now first introduced to the English reader. They are useful as a mechanical assistance in explaining the modes of combination of atoms, and their arrangement in molecules.

It will be noticed that casts of the original plates have been used, and that two or three of them contain a few words of explanation in the original language. To obviate this would have required the engraving of new plates, which was not considered necessary.

My warmest thanks are due to Dr. Stevenson for kindly undertaking the labour of revising the proof-sheets as the work passed through the press, and thereby imparting to it a guarantee of correctness and an authority which it would not otherwise have possessed.

W. C.

*Kennington Park Road, S.*
*November*, 1867.

# PREFACE TO THE FIRST EDITION.

During the last ten years great progress has been made by the science of Chemistry. New and important discoveries have succeeded one another rapidly, and at the present time great advances are being made in the art of synthesis.

In 1855 Gerhardt contributed greatly to this progress by the publication of his treatise on "Organic Chemistry." At the same time, whilst he systematized the knowledge of his epoch, other workers not less indefatigable—MM. Wurtz, Cannizzaro, Hofmann, Williamson, and several others equally ardent—contributed the results of their activity. Occasionally, it is true, their discoveries wrought important modifications in the primitive plan, but it may be affirmed that the ideas of Gerhardt have not been assailed in any essential point.

From this series of works a collection of theories has arisen upon which the chemical science of the present day is founded. These theories are taught professorially, more or less, in Germany, in England, and in Italy; but in France, where they first arose, they are not generally taught.

The greater number of chemists recognize that it is time to put an end to a system of study essentially retrograde and false; but they hesitate, remembering the little help their oral instruction will find in the number of elementary works on Chemistry which, with the old notation, propagate antiquated ideas. If these considerations did not naturally bring to our pen the name of M. Wurtz, the great sympathy which attaches us to his person, and, above all, our esteem for his character and high intellect, would suffice to dictate to us an eulogium on his excellent "Leçons de Philosophie Chimique," which he has just published.

This book marks a period: it is Chemistry making a halt in the midst of its conquests, and contemplating at the same time the road already traversed and the goal to be attained.

But a book which presents a science from so high a point of view would not be suitable for those who seek initiation into that science. The intellectual summit cannot be attained at one flight. Lower stations are necessary, and the work which we now offer to the public only pretends to be a point of departure. Although elementary, it sets forth the modern theories, and contains the indications indispensable for the guidance of those who wish to raise themselves towards the higher regions of Chemistry.

The descriptive part may appear to be too much abridged, if compared with the developments of theories which it contains. Such as it is, it will nevertheless suffice for the student, and will exceed in many points the ordinary outline of his studies.

We asked ourselves at the commencement if it would not be better to abridge the work still further, and to confine it to the application of Chemistry to Medicine; in short, to make it a Medical Chemistry; but we thought it better to abandon this first project. Physicians will not have a correct idea of those parts of Chemistry which are directly useful to them until they have studied the science as a whole. We hope to obtain this result by placing Chemistry before them in as few pages as possible; and our professorship at the Faculty of Medicine at Paris authorizes us to believe that our book will become a classical work for students of Medicine.

In our opinion students enter upon a false path when they neglect the knowledge of laws to gain for themselves simply an acquaintance with a number of facts, with which they uselessly overload the memory. Besides, special works are always at their disposal when they wish to enter upon practice; and the first element of an important manipulation is found in a judgment strengthened by a positive doctrine which understands how to devise experiments and appreciate unlooked-for results. Nevertheless, we are far from stating that the student ought to limit himself to the philosophy of Chemistry and ignore altogether the properties of bodies. But here also we would leave the beaten path. The practice is to study separately the characters of different bodies, and scarcely to notice the characteristics of a group. We shall proceed in the inverse manner. Thus, in Organic Chemistry, instead of passing the different alcohols successively in review, we shall give the characters of the Alchohol group, and follow up with the names and formulæ of the bodies which compose it. It will then be easy for the student to apply to each of them the general properties which belong to all.

This method will not prevent us pointing out, in a special paragraph following each group, the name, the properties, and the usual mode of preparation of the bodies most frequently employed, which these different groups contain.

In this manner the student having only to remember the properties of certain series, instead of large numbers of individuals, will retain them more faithfully in his memory.

Will this proceeding, which we have always found successful in special teaching, succeed in this book? We hope it will, and we place our work before the public in the full confidence that it will be appreciated.

# PREFACE TO THE SECOND EDITION.

The hopes we entertained when publishing our First Edition have been completely realized. In less than two years it has been exhausted; and, encouraged by our success, we publish this Second Edition, revised, corrected, and enlarged.

There will be found in it a more complete and detailed discussion on the questions upon which Chemists are still divided; and the descriptive part, which we were obliged to curtail in the First Edition, has been considerably increased.

After the revolution in teaching which has taken place at the Faculty of Medicine, where M. Wurtz now inculcates the new views, we think that this Edition will answer every purpose better than the preceding one.

We have endeavoured to make the theoretical demonstrations, as well as the explanations of facts, as clear as possible; to use no expression which has not already been defined and applied; and to follow the logical order which is observed in the mathematical sciences.

LEEDS SCHOOL OF MEDICINE

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# ERRATUM.

Page 396, line 33, *for* "monochlorhydrate," *read* "monohydrate."

# PRINCIPLES OF CHEMISTRY,

## FOUNDED ON MODERN THEORIES.

## PART FIRST.

### GENERAL PRINCIPLES.

### PRELIMINARY CONSIDERATIONS.

If we cast our eyes around us, we are struck by the sight of a multitude of objects of infinite variety. All these objects, whatever they may be, have received the general name of bodies. Thus the sun, the earth, my house, the chair on which I sit, the pen with which I write, the ink into which I dip my pen, and the inkstand which contains it, are all bodies.

That which constitutes bodies is called matter or substance. In speaking generally we may say that matter is whatever strikes our senses; more scientifically speaking, matter is everything that obeys the laws of gravitation.

Bodies are not formed of substance everywhere continuous in itself, as is shown by their porosity, their power of augmenting and diminishing in volume, and even of changing their condition under certain influences. They are constituted by the aggregation of small particles called molecules, placed at a certain distance from each other, and maintained in equilibrium by the forces of attraction and repulsion which they exercise towards one another.

These molecules are not the extreme limit to which it is possible to attain in the division of matter. By bringing other forces into action, they can, in the majority of cases, be subdivided into portions still smaller, to which we give the name of atoms.

In exceptional cases they are not thus divisible. In such cases we say that the molecule and the atom of these bodies are the same.

The aggregate of all bodies which exist has received the name of nature; and the study of nature is called natural philosophy.

In natural philosophy two great divisions ought first to be made.

Certain sciences study living bodies, especially the modes by which their vitality is manifested; that is to say, while investigating the laws of life they lay aside the consideration of any properties which these bodies possess in common with inorganic bodies. When they study inorganic bodies they only take cognizance of their manner of existing in nature, their external properties, without noticing the modifications which these properties may undergo under the influence of various agents. Other sciences, on the contrary, in studying inorganic bodies, seek both their external properties and the modifications which we can impress upon them by the aid of agents at our disposal. They do not occupy themselves with living beings, or at least only study the properties which these possess in common with inorganic bodies. The name of "Natural Science," properly so called, or "Natural History," is given to the first of these sciences, while the appellation "Physical Science" is reserved for the second.

Physical Science contains two distinct sciences—physics and chemistry. The science of physics studies bodies from the point of view of their properties and the actions which they exercise on each other, in so far as these actions do not affect their intimate constitution.

Chemistry, on the contrary, studies the properties of bodies and the actions which they exercise upon each other, in so far as these actions do relate to their intimate constitution.

This definition of physics and chemistry, which, with some modifications in form, is that which is found in all works, is incomplete. After saying that chemical phenomena have relation to the intimate constitution of bodies, and physical phenomena have not, it still remains to define what is meant by intimate constitution. We say that bodies are not modified in their intimate constitution when the force by which they are attacked passes between their molecules without the latter undergoing any alteration, either in the number of atoms of which they are composed, in the relative distance of these atoms, their mode of grouping, or nature.

We say, on the contrary, of a body, that it is modified in its intimate constitution when its molecule is altered in the nature, the number, the distance, or the mode of grouping of the atoms which it contains.

Thus: all the phenomena in which the molecule remains unaltered belong to the domain of physics; all those, on the contrary, in which the molecule is more or less modified, appertain to the domain of chemistry.

To render this definition quite clear, we will give an example of these two orders of phenomena. If we take soft iron, and submit it to the action of an electric current, the iron acquires all the properties of a magnet. Interrupt the current, and the metal will regain all its original properties. Its molecules will not have undergone any alteration; the modification observed for an instant has not affected its intimate constitution. This is a physical phenomenon. If, on the contrary, we warm a piece of phosphorus, protected from the air for a sufficient length of time, and at a temperature of about 240°; from being yellow, transparent, very inflammable, and soluble in certain solvents as

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it was, it becomes red, opaque, less inflammable, and insoluble in the same solvents, and keeps its new characters when completely cold. The modification produced by the influence of heat affects its intimate constitution. This is a chemical phenomenon.

In chemistry bodies are divided into two great classes—simple and compound. Simple bodies are those from which we are as yet only able to extract one kind of matter. Compound bodies are those which we are able to resolve into two or more substances possessing different properties. Our belief that a body is simple cannot be positive ; those regarded as simple to-day, may to-morrow be proved to be compound.

Among compound bodies there are some which consist of simple mixtures, and others which are the result of definite combination. They are distinguished by two principal characters:

1st. In mixtures each element may bear any proportion to the others. In compounds which result from combination, the proportion is definite and constant.

2ndly. In mixtures all the elements retain the properties that are peculiar to them. In compounds resulting from combination, each element loses the properties that characterize it to acquire new ones common to all. We have really a new body—thus:

*Sulphur* is soluble in sulphide of carbon, and iron is attracted by the magnet. If iron and sulphur are reduced to powder and mixed, they will retain their properties. The iron can be separated by means of the magnet, and the sulphur by dissolving it in sulphide of carbon. If, however, the mixed powders were to be heated, a chemical action would ensue. The mass would become black, and assume new properties; it would no longer be attracted by the magnet, as was the iron, nor soluble in sulphide of carbon, as was the sulphur. Before bringing the heat into action there was a simple mixture ; now there is a definite combination.

When combination is produced, the observer perceives it by certain phenomena : there is always disengagement of heat, and development of electricity ; sometimes the production of light, and often contraction of the mass.

Combination is favoured by heat, light, electricity, the nascent state, attractive force, bulk, and a certain elective property, in virtue of which a given body combines more readily with a second than it will with any other.

1st. **Heat.**—In the effect which heat produced upon the mixture of iron and sulphur, we have already witnessed the intervention of this agent.

2ndly. **Light.**—The action of light is often indispensable. Thus the presence of a violet ray suffices to determine the sudden combination of chlorine and hydrogen, which cannot take place in total darkness.

3rd. **Electricity.**—That this has an action can no longer be doubted. It has been demonstrated in a startling manner by the direct combination of carbon and hydrogen realised by M. Berthelot. This combination, which cannot take place at any temperature without the electric action, easily occurs under the influence of a strong current.

4th. **The Nascent State.**—We mean by this the state in which bodies exist at the instant they are set free from a combination. Experience proves that in this condition they have a greater tendency to combine than when they are taken in the free state.

5th. **Action of Bulk.**—Of this description are actions in which two bodies mutually displace each other in a combination, the one which is in larger quantity taking the place of the other. M. Deville has recently given a very rational explanation of the actions of bulk. From his experience, he has arrived at the conclusion that in the decomposition of bodies by heat, phenomena take place analogous to those which are observed in the vaporization of liquids. Just as the passage of a liquid into the gaseous state requires a certain amount of heat which is entirely absorbed, so, to reduce a compound body to its elements, there is required the absorption of a quantity of heat equal to that which was disengaged in its formation.

When a liquid is heated to a temperature lower than its boiling point it emits vapour. After a time the space in which it is contained becomes saturated, when the vaporization ceases, the pressure of the vapour already formed counteracting the tendency which the remainder of the liquid has to become vaporized. An analogous phenomenon is observed in decompositions. When a compound body is heated to a temperature insufficient to cause its complete decomposition, a part, nevertheless, is resolved into its elements, but the quantity is only a small proportion of the whole. The decomposition presently stops. This equilibrium is produced when the decomposition which takes place is exactly compensated by the reconstruction which goes on at the same time.

Let us suppose that we heat the vapour of water to 120° in a great excess of chlorine (water is composed of oxygen and hydrogen), a small quantity of hydrogen and oxygen will become free. Hydrogen has a tendency to combine both with oxygen and chlorine; but the oxygen being small in quantity compared to the chlorine, it is with the latter body that the greater part of the hydrogen will combine. The phenomenon will be thus continued, and consequently more of the water will be destroyed than will be reconstituted, and the greater part of the water will in a certain time be found transformed into hydrochloric acid (composed of hydrogen and chlorine). If, on the contrary, we heat hydrochloric acid in a large quantity of oxygen, the oxygen being always in great excess relatively to the chlorine, then it will be with the oxygen that the greater part of the hydrogen set free by the decomposition of the hydrochloric acid will combine. Thus hydrochloric acid will be almost entirely transformed into water. In a word, the same phenomena will again have taken place, but in the inverse order.

6th. **Catalysis.**—This name is applied when a body determines a combination or a decomposition simply by its presence alone, without intervening in the reaction.

7th. **Elective Properties.**—The elective properties, in virtue of which bodies have more or less tendency to combine with one another, are matters of experience. They belong to the intimate nature of bodies. We are usually able to foresee them, from the following circumstance: when two bodies combine the compound can be reduced to its elements by the influence of an electric current. In this case one of the constituent principles goes to the positive, the other to the negative pole. We suppose the former—that which goes to the positive pole—to be charged with negative electricity; and it is called electro-negative in relation to the second, which we suppose charged with positive electricity, and which is called electro-positive. All simple bodies can be ranged in such a series that each of them will be electro-positive towards those which precede it, and electro-negative towards all those which follow.

Experience proves that the tendency which any two bodies have to combine with one another is in direct proportion to the distance which separates them in the electric series.

We have already seen that in order to understand the different physical and chemical phenomena we are obliged to suppose that matter is composed of particles indivisible by means of the forces at our disposal—particles which are called molecules or atoms.

Further, we have seen that these two words are far from being synonymous, the molecule being generally constituted by an aggregation of atoms. The force that unites the atoms in the molecule has received the name of affinity; that which unites the molecules among themselves is called cohesion. Formerly affinity was defined as the force which unites the atoms of several different substances. This definition was incomplete. The force which unites two atoms of hydrogen in the molecule of this body is as much affinity as that which unites an atom of hydrogen to an atom of chlorine in the molecule of hydrochloric acid.

In consequence of this false definition the word affinity presents, besides the philosophical meaning which we have just stated, a different meaning. We call affinity the elective property of which we have just spoken, and in virtue of which certain bodies are more or less apt to combine. It is thus that we say that chlorine has great affinity for hydrogen. We call a compound body stable when it easily resists decomposing agents. In the contrary case it is called unstable. Two bodies, A and B, can often form several definite combinations into which they enter in variable proportions. If we take from each such a quantity that it contains a constant weight of the body A, the weights of the substance B will always be in relative proportion to it. Thus the quantity of A contained in different weights of each of the compounds that it forms with B, being 1, those of B will be respectively

$$1 : 2 : 3 : 4 : 5 : 6 : 7.$$

Similarly, the weight of A being 2, those of B will be

$$2 : 4 : 6 : 8 : 10,$$

and so on. This law has received the name of the *law of multiple proportions*, and is due to Dalton. When the combining bodies exist in the gaseous state there is always a simple proportion between the volumes of the two primitive gases and the volume of the compound formed, taken in the vapour state under the same conditions of pressure and temperature.

The compound often occupies a smaller volume than the sum of the volumes of the elementary gases. Then we say there has been a contraction. This contraction can be expressed by the general formula $\frac{V-v}{V}$, where V represents the volume of the mixture of the two gases, $v$ the volume of the compound formed. Sometimes the compound occupies the same volume as the sum of the two elementary gases: this case does not occur except when the two elementary gases combine in equal volume: the inverse is not correct; there may be contraction even when two gases combine in equal volumes.

The volume of the compound formed never surpasses the sum of the volumes of the elementary gases; that is to say, there is never dilatation. This law is called the "law of Gay-Lussac."

## CRYSTALLOGRAPHY—OPTICAL PROPERTIES.

**Crystallography.**—Most substances take geometrical forms when they pass from the liquid or gaseous to the solid state with sufficient slowness to enable their molecules to take the positions natural to them. These forms, which are always the same when they are produced in the same conditions, have received the name of crystalline forms, and the bodies which assume them that of crystals. Crystals never have retiring angles. Such angles are only found in groups of several crystals joined together. Sometimes these joinings take place with so much symmetry that the groups which result present a very regular appearance.

Crystals do not break with equal facility in every way. Generally they possess two or three directions in which fracture is easily accomplished, and following plane faces parallel to one another. These parallel faces are called cleavages. When we cleave crystals in a direction contrary to the proper line of cleavage, new forms are obtained, which have been called cleavage forms. In crystals we distinguish *faces*, such as are bounded by the lines A B C D, A B E F (fig. 1); *edges*, or lines formed by the junction of two faces, A B, C D; and *angles*, which result from the intersection of three or more faces, as the angle A B D E, from the intersection of the three faces A B C D, A B E F, and B D E G.

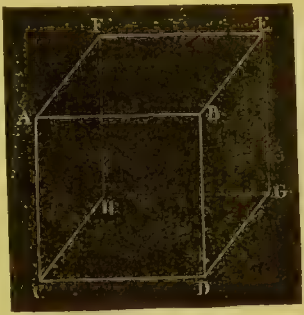


Fig. 1.

If we study attentively the different crystalline forms which are found in nature, we see that many are derived from one by a very simple law. The collection of all the forms derived thus from one typical form has received the name of "crystalline system." There are six crystalline systems; that is to say, six groups, of which each comprises forms which one derives from the others, and can in no way derive from those that are placed in the five other groups.

These six systems can be arranged in two classes: the first containing all the forms in which the three edges that arise from the same angle are perpendicular to one another; the second contains, on the contrary, all the forms in which the three edges are not placed at right angles to each other.

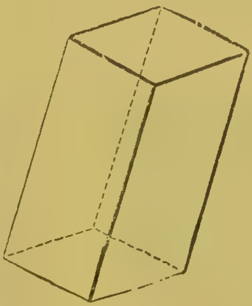


Fig. 2.

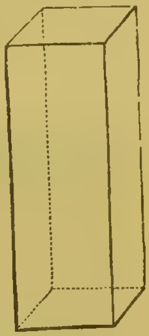


Fig. 3.

Class First. *Perpendicular Edges.*—This class contains three systems of crystals, which are distinguished from each other by the following characters:

In the *first system* the three edges are of equal length. This is the cubic or regular system (fig. 1).

In the *second system* two of the three edges are of the same length, but the third is a different length to the other two. This is the system of a *right prism with a square base* (fig. 2).

In the *third system* the three edges are unequal. This is a system of a *right prism having a rectangular base* (fig. 3).

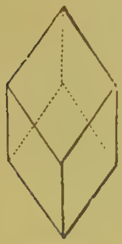
Class Second. *Oblique Edges.*—In this class the three last crystalline systems are ranged; they are distinguished from each other by the same characters which served to determine them first.

In the *fourth system* the three edges are of the same length. This is the *rhombic* system (fig. 4).

In the *fifth system* two out of the three edges are of an equal length; but the the third has a different length from the others. This is the system of an *inclined prism having a rhombic base.*

In the *sixth system* the three edges are unequal. This is the system of *an inclined prism having its base a parellelogram*, or the irregular system (fig. 6). The typical forms of which these six systems are the bases undergo modifications, by the help of which secondary forms are derived.

These modifications consist in the substitution of an edge or an angle of a crystal by one or more faces which take the name of truncated faces. If the truncated faces which affect the edges, or those which affect the angles, are prolonged until they touch each other, a second form, derived from the first, will be obtained. It is thus that in substituting each angle of the cube by a face equally inclined on each edge, and prolonging all the faces, that we obtain the regular octahedron, as is shown by figs. 7, 8, and 9.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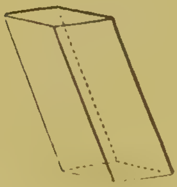
Fig. 5.

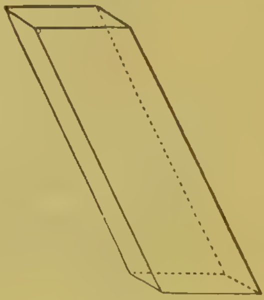
Fig. 6.

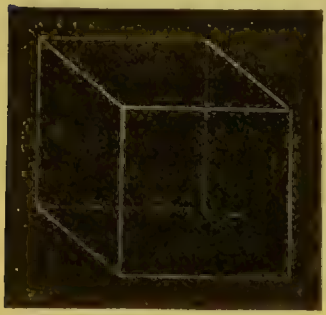
Fig. 7.

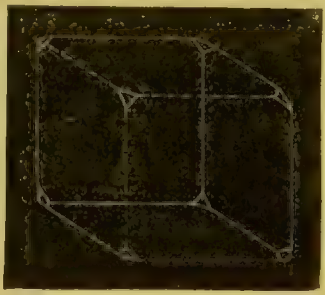
Fig. 8.

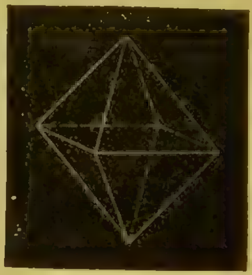
Fig. 9.

When the truncated faces are not prolonged, the crystal contains at the same time both faces of the primitive solid, and faces of the derived solid. Then we have a compound form, such as the octahedral cube of fig. 8.

The law which presides over the modifications of which we have just spoken is known as *the law of symmetry.* It is thus expressed :—In a crystal all the similar parts must always be modified in a similar manner. It is for this reason that in a cube where all the edges are alike, and where all the angles are alike, a modification on one edge, or on one angle, necessitates the like on all the other edges or angles.

There are nevertheless special cases in which only half of the parts which ought to be modified are really so, only one of the two alternative parts having undergone the modification. Crystals of this nature are called hemihedral. When we examine them, we find that the truncated facets, which are then called hemihedral facets, are situated always to the right or always to the left of the observer whichever way we turn the crystal. When the facets are to the right, we say that the crystal is hemihedral to the right; when they are to the left, it is

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hemihedral to the left. Certain substances assume crystalline forms, if not quite identical, at least so nearly so that they are only to be distinguished by a very precise measurement of angles, and these angles are very much alike. If such substances were crystallized together they would enter into one crystal in different proportions, and the angle of the crystal would be intermediate between those of the different bodies which take part in it. The substances which possess this property are called isomorphous.

**Optical Properties.**—When a ray of light is reflected under a certain angle, or is refracted in passing through the crystals called double refracting, it becomes polarized. We understand by this word that it acquires the property of extinguishing itself every time it is reflected or refracted in such condition that, if it was not already modified, it would pass and take a plane perpendicular to that which it has already.

When a polarized ray falls on a double refracting crystal, under conditions suitable for it to be extinguished, it can be made to reappear by interposing in its passage tubes full of particular solutions, or a sheet of certain transparent substances. The ray can again be extinguished if the double refracting crystal be turned a certain number of degrees either to the right or to the left. Then we say that the interposed substance turns the plane of polarization to the right or left; that it is dextrogyrate or levogyrate. Speaking generally, a substance which acts upon light in the manner described is said to be active, whatever may be the way in which it acts.

When an active substance is capable of crystallization, there is a relation between the crystalline form and the direction of deviation. This relation is such that, on inspection of a crystal, we are able to say whether the body which constitutes it is active, and whether it is levogyrate or dextrogyrate. In fact all active substances, in crystallizing, assume hemihedral forms; and it is remarked that those which turn the plane of polarization to the right are hemihedral to the right, while those that turn it to the left are hemihedral to the left. This remarkable discovery—suspected first by Herschel—has been definitely placed in the ranks of science by the labours of M. Pasteur.

## EQUIVALENTS.

If we dissolve in water a compound of chlorine and mercury (chloride of mercury), and place a sheet of copper in the solution, the metallic sheet will become white, while the solution becomes blue, and that without throwing off the smallest quantity of chlorine. After a certain time, on taking out the metal and warming it in an apparatus which permits the volatile parts to be collected, a certain weight of metallic mercury is obtained, and the sheet of copper regains its natural colour. If it be then weighed, and its present weight be deducted from that which it possessed before the experiment, it will be found to have sustained a loss indicating the disappearance of a certain quantity of copper. On examining the solution which has become blue, by the proper chemical tests, we find that it contains copper, but that it does not now contain the smallest trace of mercury.

In comparing the weights of the mercury precipitated with the copper dissolved, we find that the 100 parts of mercury have been replaced by 31·50 parts of copper; this proportion always remaining strictly the same, whatever may be the absolute reacting quantities of the two metals. Let us, in the second place, take a sheet of iron and plunge it into the copper liquor, from which the mercury is entirely extracted; the copper will be precipitated in its turn, and the iron will enter into solution. On ascertaining the amount of iron dissolved, it will be found that 31·50 parts of copper have been replaced by 28 of iron; this proportion always remaining the same, under all circumstances, without our being able to observe the least disengagement of chlorine.

Again, let us take 28 parts of iron, and place them in a compound of chlorine and hydrogen (hydrochloric acid); hydrogen gas will be disengaged, and the iron will take its place. If the gas, set at liberty during the solution of the 28 parts of iron, be collected, the weight can be obtained by measuring the volume (we know that 1 litre of hydrogen weighs 0·0896), and that this weight will be equal to 1. From the foregoing it results, that 100 of mercury having been replaced by 31·50 of copper, and these, in their turn, by 28 of iron, without the quantity of chlorine contained in the solution having varied, 28 of iron are equivalent to 31·50 of copper, and to 100 of mercury.

Moreover, as 1 of hydrogen has been replaced by 28 of iron, these two quantities are still equivalent; and, finally, as things which are equal to the same thing are equal to one another, it follows that 1 of hydrogen equals 100 of mercury and 31·50 of copper: that is to say, 100 of mercury, 31·50 of copper, 28 of iron, and 1 of hydrogen are equal. The numbers which thus express the proportions according to which the bodies replace each other in chemical combinations bear the name of equivalents, or proportional numbers; and thus we say that the equivalents of hydrogen, mercury, iron, and copper, are respectively 1, 100, 28, 31·50.

In these proportions hydrogen has been taken as unity, because of all known bodies its equivalent is the lowest.

**Determination of Equivalents.**—The preceding method is neither applicable to all simple bodies, nor sufficiently precise. There exists another, by the help of which we can determine exactly the equivalents of all bodies. To find the equivalent, say, of potassium, relative to hydrogen taken as unity, we first combine potassium with chlorine, and thus obtain a compound called chloride of potassium, which we analyze. This analysis shows that 100 parts of the chloride contain 47·65 of chlorine and 52·35 of potassium.

Then we combine chlorine with hydrogen; and, on analyzing the hydrochloric acid thus produced, we find that it contains, in 100 parts, 97·26 of chlorine and 2·74 of hydrogen. Then we take such a quantity of each of these compounds that they contain the same weight of chlorine. Let this weight be 35·5; that is to say, that which in hydrochloric acid is combined with 1 of hydrogen (which we find by the proportion—

$$2{\cdot}74 : 97{\cdot}26 :: 1 : x; \text{ therefore } x = 35{\cdot}5).$$

The quantity of hydrochloric acid containing this weight of chlorine will be 36·5. The weight of chloride of potassium, which also contains 35·5 of chlorine, is given by the proportion—

$$47{\cdot}65 : 100 :: 35{\cdot}5 : x; \text{ therefore } x = 74{\cdot}50.$$

Therefore 74·50 of chloride of potassium and 36·5 of hydrochloric acid contain equally 35·5 of chlorine; and as 36·5 of hydrochloric acid contain 1 of hydrogen, and 74·50 of chloride of potassium contain 39 of potassium, 1 of hydrogen and 39 of potassium are equivalents; the equivalent of hydrogen being 1, that of potassium is therefore 39.

It is evident that, instead of taking the equivalent of the potassium with regard to hydrogen in a direct manner, we can arrive at it in a more indirect way. It would suffice to determine by the same method what is the quantity of potassium which is equal to 28 of iron, or to 100 of mercury, or to 103·5 of lead, etc.; and as 103·5 of lead, 100 of mercury, 28 of iron, each equal 1 of hydrogen, the number found would be the real equivalent of potassium; that is to say, 39.

Thus, to determine the equivalent of an element A, we combine it with another body B; then we take a compound of this second body B with a third body C, of which the equivalent is known, and we seek what is the quantity of B which is there combined with an equivalent of C. Let P be this quantity of B. Lastly, the analysis of the compound A + B being made, we calculate what is the weight of A which is there united to a weight of B equal to P; this weight of A represents its equivalent.

Nevertheless, this method possesses an inconvenience and often would not give a precise result, if Mitscherlich had not completed it by a remarkable discovery. It is excellent in cases which require to determine the equivalent of elements which only form one series of combinations, but would cease to be applicable to those which, with a single simple body, form different orders of compounds.

For example, silver forming only one order of well-defined compounds, its equivalent can be determined by the above process, and has been found equal to 108; but this result could not be arrived at if the same method were used to determine the equivalent of copper.

Copper forms with chlorine (as well as with the greater part of the bodies with which it is capable of combining) two compounds; one, called protochloride, contains in a hundred parts—

| | |
|---|---|
| Chlorine . . . . . . . . | 36·04 |
| Copper. . . . . . . . . . | 63·96 |
| | 100·00 |

The second, called bichloride, contains—

| | |
|---|---|
| Chlorine . . . . . . . . | 52·95 |
| Copper . . . . . . . . . | 47·05 |
| | 100·00 |

If we wish to decompose the protochloride in order to determine the equivalent of copper, in comparing this compound with chloride of silver, knowing the latter contains—

| | |
|---|---|
| Silver . . . . . . . . . . | 75·26 |
| Chlorine . . . . . . . . | 24·74 |
| | 100·00 |

and that the equivalent of silver is 108, we calculate first what is the quantity of chlorine, which, in the chloride of silver, is combined with 108 of silver, which is given by the proportion—

$$75{\cdot}26 : 24{\cdot}74 :: 108 : x; \text{ therefore } x = \frac{24{\cdot}74 \times 108}{75{\cdot}26} = 35{\cdot}5.$$

In the second place we calculate the quantity of copper which, in the protochloride of this metal, is combined with 35·5 of chlorine, and by the proportion—

$$36{\cdot}04 : 63{\cdot}96 :: 35{\cdot}5 : x; \text{ therefore } x = \frac{63{\cdot}96 \times 35{\cdot}5}{36{\cdot}04} = 63,$$

the equivalent of the copper.

If, on the contrary, we wished to decompose the bichloride of copper in order to determine the equivalent of the metal, we should calculate the quantity of this body which, in the bichloride, is united to 35·5 of chlorine. The following would be the proportion—

$$52{\cdot}95 : 47{\cdot}05 :: 35{\cdot}5 : x$$

$$\text{therefore } x = \frac{47{\cdot}05 \times 35{\cdot}5}{52{\cdot}95} = 31{\cdot}50 = \frac{63}{2}.$$

The number 31·50 would thus represent the equivalent of the copper.

Thus, if we compared either of the two chlorides of copper with chloride of silver, we should find two different equivalents for the copper, of which one is double the other, and we could only choose arbitrarily between them. Mitscherlich, however, has found a law which removes all uncertainty from the application of this method.

This chemist has discovered that isomorphous bodies have a similar constitution, and he has thence concluded that only isomorphous bodies should be compared together. If we apply this rule to the preceding case, we see that protochloride of copper alone being isomorphous with chloride of silver can alone be compared with it. Thence, the true equivalent of copper will be that which is deduced from this comparison; that is to say, 63.

Before Mitscherlich's law became known, the equivalent of copper had been arbitrarily deduced from the composition of the bichloride of the metal; thence the equivalent 31·50, which we still find in most of the elementary books, though it is incorrect.

Nevertheless, it results from the preceding facts, that the term "equivalent" is wanting in precision; in reality, we ought to say that a simple body has as many equivalents as it makes combinations with any other element. It is clear that if, in the protochloride of copper, 63 of copper being combined with 35·5 of chlorine, take the place of 108 of silver, so also, in the bichloride, 31·50 of the same metal are united to 35·5 of chlorine, and, consequently, equally take the place of 108 of silver. This confusion will disappear if, for the term equivalent, we substitute the much more clear and precise one, "atomic weight."

## ATOMIC THEORY.

Dalton was the first who conceived the idea of explaining combinations by the hypothesis of atoms in juxtaposition. He thence deduced that these atoms being indivisible, the different quantities of a body A which unite with an invariable quantity of another body B ought to be in the same rational and commensurable proportions. An atom of the substance A, according to this hypothesis, can only be in juxtaposition with a number of entire atoms of the substance B. From the atomic hypothesis, therefore, Dalton deduced, *à priori*, the law of multiple proportions; a law which, after having received the sanction of experience, has become one of the most solid foundations of this hypothesis.

The atomic theory well explains the fact of equivalents; that is to say, the fact that bodies enter into combinations in quantities which assume the same proportions, though varying with each case.

Suppose, for example, that an atom of potassium weighs 39 times as much as an atom of hydrogen, and that an atom of chlorine, in order to form a definite combination, requires an atom of one or other of these bodies. The weight of the atom of chlorine remaining the same in both cases, it is evident that, to saturate it, would require 39 times more weight of potassium than of hydrogen. Further, as these relations cannot change, when the combination, instead of taking place between two atoms, takes place between an undetermined number of atoms it results that, to saturate any quantity whatsoever of chlorine, takes 39 times more of potassium than of hydrogen: this is what we have already expressed in saying that the equivalent of potassium is 39 relative to that of hydrogen taken as 1. In the atomic theory the equivalents of bodies become, therefore, the weight of their atoms, compared to the weight of the atom of hydrogen taken as unity, and they assume the name of atomic weights.

The idea of atomic weights has nevertheless, as we said before, something more precise than that of the equivalent. It is still a proportion, but a proportion better determined. Thus, let us suppose that an atom of oxygen acts the same part as an atom of hydrogen; in a word, that the two bodies may be substituted atom for atom; experience shows that 8 parts by weight of oxygen replace 1 of hydrogen, and we must conclude from this that the atom of oxygen weighs 8 times as much as the atom of hydrogen; that the atomic weight of oxygen is 8.

Now, let us admit that to replace 1 atom of oxygen requires 2 of hydrogen. As 1 of hydrogen is replaced by 8 of oxygen, 2 will be replaced by 16, which will bring us to the conclusion that the atom of oxygen weighs 16 times more than that of hydrogen; that the atomic weight of oxygen is 16. Therefore, as the atom of oxygen is substituted either for 1 or for 2 atoms of hydrogen, the atomic weight of the first of these bodies is 8 or 16, while the equivalent, which only represents a simple ponderable relation without consideration of atoms, always remains equal to 8. At the same time as the atomic weights, we ought also to consider the molecular weights; that is to say, the weights of the molecules of bodies, simple or compound, in proportion to that of hydrogen taken as 1.

Compound bodies cannot have atomic weights; they have a molecular weight. Simple bodies have both a molecular and an atomic weight. These two weights may be confounded in special cases where the molecule only contains one atom.

By knowing the atomic weights of all simple bodies, and the molecular weights of these elements, and of the compounds which they form, we shall have much more exact ideas of the constitution of bodies than if we contented ourselves with the mere knowledge of equivalents. There are means by the aid of which we can arrive at this knowledge.

**Molecular Weights.**—In the gaseous state, all bodies, whether simple or compound, have the same co-efficient of dilatation; that is to say, they expand equally by an equal increase of temperature: all can be equally compressed under the same circumstances; that is to say, they are reduced to the same fraction of their volume by the same increase of pressure, everything being equal.

The elastic force of gases is, therefore, about the same in all, and as it is generally allowed that gaseous molecules are in movement, and that the elastic force of gases results from the shock of their molecules against the sides of the vessels containing them, the most simple way of explaining that they all have the same elastic force under the same conditions consists in admitting that, in equal volumes, the pressure and temperature being the same, all gases contain the same number of molecules. This supposition is based on the law of Gay-Lussac, relative to the combinations of gaseous substances. If gaseous bodies are

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formed of molecules, if the decompositions and combinations result from the exchange of atoms which takes place between the molecules, or, again, from the union of several of these molecules into one, it is very evident that the number of molecules which have reacted, and the number of those which arise from the reaction, ought to present a simple proportion. In effect, reactions can only be produced between one molecule and another, or between one molecule and two others, and so on. Thus, if in equal volumes, and under the same conditions of pressure and temperature, all gases contain the same number of molecules, the simple proportion which ought to exist between the number of the reacting molecules and the number of molecules formed in the reaction ought to be equally observed between volumes of the gases before and after the reaction, which really takes place. This hypothesis that, for an equal volume, all gases contain the same number of molecules, first brought forward by Avogadro, and afterwards developed by Ampère, is best known under the name of the latter.

Starting from this principle, if we compare equal volumes of chlorine and hydrogen, we find that the volume of chlorine weighs 35 and a half times more than that of hydrogen; we therefore conclude that the molecule of chlorine weighs 35 and a half times more than the molecule of hydrogen. But, as we shall see presently, the molecule of hydrogen is composed of 2 atoms. Hence the atom of hydrogen weighs only half as much as its molecule; and as a molecule of chlorine weighs 35 and a half times as much as a molecule of hydrogen, it will weigh 71 times as much as an atom of the same body. If we take the weight of the atom of hydrogen as unity in molecular weights, as we have done in atomical weights, we should, therefore, say that the molecular weight of chlorine is 71.

Thus we obtain the molecular weight of a simple or compound body by taking its vapour density relative to hydrogen, and multiplying by 2. As we usually compare the densities of vapours relatively to air, and as air weighs 14·435 times more than hydrogen, the density relative to air must be multiplied by 14·435 in order to transform it into the density relative to hydrogen. Finally, in order to obtain the molecular weight of a substance, the number which indicates this last density must be doubled; it is easier to multiply the density relative to air by the double of 14·435; that is to say, by 28·87. Thus the molecular weight of a substance is obtained on multiplying by 28·87, its vapour density taken relative to air.

If all bodies were volatile, nothing would be easier than to determine their molecular weights, but such is not the case; a number of compound bodies are decomposed before attaining the temperature at which they are transformed into vapour; thence the necessity of a different method of determining molecular weights. Either these bodies are capable of entering into combination with other bodies, or they are not. Let us take the first case, and, as an example, stearic acid. This acid is a fatty body, which is not perceptibly volatile, and in which a certain weight of potassium is capable of being substituted for an equivalent weight of hydrogen. This compound has very analogous properties to acetic acid, which can also undergo the substitution of a part of its hydrogen by potassium, and of which we can determine the molecular weight, as it is volatile.

We prove by experiment that the molecular weight of acetic acid is 60, and that in 60 parts of this acid 1 of hydrogen can be replaced by 39 of potassium. If we then seek the quantity of stearic acid which, on losing 1 of hydrogen, can combine with 39 parts of potassium, we find that this quantity is equal to 284.

Thus 284 parts of stearic acid are the equivalent of 60 of acetic acid; and, as 60 of acetic acid represent the weight of the molecule of this acid, 284 ought also to represent the weight of the molecule of stearic acid.

This method only gives exact results when the bodies compared have the same molecular constitution. Thus an acid like acetic acid could not be compared with citric acid, or, at least, considerations of another order must be brought to bear in the comparison.

To obtain the molecular weight of a substance non-volatile, but capable of combining with other bodies, it suffices to determine what is the quantity of this substance which equals the known molecular weight of a volatile body of the same constitution. This quantity represents the weight of its molecule.

Lastly, if the non-volatile substance is incapable of entering into combination, it is submitted to the action of reagents which decompose it. We then obtain new compounds, of which the molecular weight can be determined by one of the preceding methods. Then we seek to trace back from the molecular weight of these latter compounds to that of the primitive body, by taking as its molecular weight that number which permits the reaction to be expressed in the most simple manner. This proceeding gives less certain results than the preceding ones, to which we always recur in preference when we are able.

If we take as unity for the volume of gases the volume of that quantity of hydrogen of which the weight corresponds to our unit of weight, it is clear from the preceding that the weight of the same volume of any simple or compound body whatsoever, considered at the gaseous state, will represent its vapour density relative to hydrogen, and consequently the half of its molecular weight. To obtain the molecular weight of a body, therefore, it is sufficient to multiply by 2 the weight of a volume of its vapour, or, what is the same thing, the molecular weight of a body will be equal to the weight of two volumes of its vapour. We express this fact when we say that all bodies have a molecular weight which corresponds to 2 volumes of their vapour.

It is evident that, if we took as unity a volume half the size of the preceding, the molecular weights of all bodies would correspond to 4 volumes of vapour.

Most modern chemists, to avoid complication, use the number 2; but older writers employed the number 4, and some elementary authors use it at the present time.

Formerly the theory of Ampère was not the principle used to determine molecular weights.

Many of these weights were incorrectly known, and were stated in treatises on chemistry at half of their proper amount. At that time there were bodies of which the molecular weight was supposed to correspond to 2 volumes, and others to 4. It is to Gerhardt that the honour of having brought into use the theory of Ampère belongs, as he showed that all molecular weights ought to correspond to the same gaseous volume, 2 or 4 volumes, according to the unit adopted.

There are nevertheless compound bodies, such as hydrated sulphuric acid and hydrochlorate of ammonia, which seem to prove exceptions to this law; their molecular weight nevertheless can in no way be divided: this could only be done by dividing at the same time the atomic weight of the simple bodies which constitute them, and these atomic weights are too surely established for it to be possible to modify them; nevertheless the vapour density of these compounds is such that their molecular weight corresponds to 4 or 8, and not to 2 or 4 volumes of vapour.*

To explain this anomaly, many chemists have thought that in the cases in question there is disunion; in other words, they suppose that, under the influence of heat, the bodies which present anomalous vapour densities decompose into two others, each occupying the volume which the primitive body would have occupied if it had not been decomposed, that is to say, 2 volumes. The two bodies united, therefore, occupy, according to this hypothesis, a volume the double of that there would be reason to expect if the compound, the vapour density of which we determine, did not decompose; and if the two bodies separated by heat are able to again unite on cooling, the experimenter will perceive nothing and believe that he has found an anomalous density.

As an example, I will take the case of chloride of ammonium, as it is really on it that all the discussion turns; and when the question is settled for it, it will be for all that resemble it. When we heat a molecule of chloride of ammonium (a compound of chlorine, hydrogen, and nitrogen) it decomposes into a molecule of hydrochloric acid (a compound of chlorine and hydrogen) and a molecule of gaseous ammonia (a compound of hydrogen and nitrogen). The number of molecules becoming double, the volume occupied by the vapour ought also to double. Then when the mixture of hydrochloric acid and gaseous ammonia becomes cold, the two bodies would again enter into combination, and the two molecules would reunite into one. If this were the case, the bodies which present anomalous densities would simply be bodies which would not volatilize without decomposition. This theory was at once attacked by M. Deville, who remarked that gaseous ammonia decomposed when heated alone, at the temperature at which the vapour density of the chloride of ammonium had been determined. Then, said he, if when the chloride of ammonium be vaporized this salt becomes decomposed, the gaseous ammonia arising from the disunion would decompose in its turn into hydrogen and nitrogen, and the chloride of ammonium would not be re-formed on cooling. This salt would not be produced when placed in contact with nitrogen, hydrogen, and hydrochloric acid. M. Wurtz replied to this objection that, in a multitude of cases, compounds which, alone, are instable, acquire stability in presence of other bodies with which, nevertheless, they do not enter into combination. He thence concluded that, probably, if gaseous ammonia does not decompose when the vapour density of chloride of ammonium is taken, it is owing to the fact that the hydrochloric acid with which it is mixed gives it stability, though not combined with it. Shortly after this M. Pebal, with the help of a very elegant apparatus, proved that the vapour of chloride of ammonium contains free gaseous ammonia. The question seemed to be decided in favour of the disunion, but, nevertheless, such was not the case. M. Deville demonstrated that a body may become partially separated before being at the temperature where it decomposes completely, and that this separation, though it may be made evident by appropriate means, may, nevertheless, be so slight as to have no influence on the results of the determination of a vapour density. Thus the question was still undecided. To settle it M. Deville performed a very ingenious experiment. He made gaseous hydrochloric acid and ammonia gas to pass into a glass globe heated by the vapour of mercury, that is to say, to 350°, a temperature at which the density of the chloride of ammonium corresponds to 4 volumes. The two gases before meeting had circulated in spiral tubes placed in the mercurial vapour, and possessed, in consequence, exactly the temperature of 350°. In these conditions their meeting produced a disengagement of heat.

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* 4 or 8, 2 or 4, represent the same thing, because of the different units of the volume adopted. These differences oblige us always to employ two numbers instead of one, of which the one is the double of the other: instead of saying 2, we say 2 or 4.

M. Deville believed he was able to deduce from this experiment that at 350° chloride of ammonium does not decompose. A body not being able to form under conditions where it is destroyed, if this salt became decomposed at 350°, it would not form at that temperature; the gaseous ammonia and hydrochloric acid would not combine under these conditions, and, consequently, no disengagement of heat would take place. As, in fact, heat *is* disengaged, we are obliged to admit that the two gases are combined at 350°, which proves that the compound they form is not decomposed at this temperature.

The argument seemed conclusive, and for a little time was believed to be decisive; it seemed no longer possible to sustain the theory of separation; but M. Lieben, in a very lucid and interesting communication to the Société Chimique of Paris, again reopened the question.

M. Lieben demonstrated by a number of examples that when a decomposition takes place by heat, and the products of this decomposition are not removed as they form, the decomposition is never complete; there always remains a small quantity of the original substance undecomposed, which produces a kind of molecular equilibrium.

He then said that if the experiment be reversed, if, instead of decomposing a body, the products of such decomposition be brought into contact at the same temperature, the equilibrium produced would still be the same, for it would be absurd to suppose that two different equilibriums can exist in identical conditions. The greatest part of the bodies brought into contact would therefore remain free, but a very small fraction of their masses would enter into combination with disengagement of heat.

By applying these arguments to M. Deville's experiment, it may be said, according to M. Lieben, that the greatest part of the two gases remain separated in this experiment, and that the portion of chloride of ammonium formed is so small as not to influence the vapour density.

It is true that the contrary may also be said, and that between these two views it is impossible to decide *à priori*; but M. Lieben's explanation proves that it is not sufficient to resolve the question to demonstrate that the meeting of gaseous ammonia and hydrochloric acid at 350° produces a disengagement of heat; this disengagement must also be measured. M. Lieben has therefore established that M. Deville's experiment proves nothing for or against the theory of separation, and that, until a stricter demonstration to the contrary occurs, this hypothesis may still be admitted to explain the anomalous vapour densities. Finally, M. Wurtz's recent works on hydrochlorate of amylene [a compound of hydrochloric acid and amylene (carbon and hydrogen)], and on hydrobromate of amylene [composed of amylene and hydrobromic acid (bromine and hydrogen)] (see *Pseudo-alcohols*), have given a clear confirmation of M. Lieben's theory.

When the vapour density of these bodies is determined at a sufficiently low temperature, these densities correspond to two volumes according to Ampère's law, and they are, moreover, normal, because they remain constant between sufficiently extended limits of temperature; 94° — 194° for hydrochlorate of amylene.

On the contrary, when a certain temperature is exceeded, these bodies begin to separate, the hydrochlorate into hydrochloric acid and amylene, the hydrobromate into amylene and hydrobromic acid; their vapour density then becomes less, and a time arrives when the separation being about complete, the density observed seems to correspond to 4 volumes. On cooling, the separated elements again unite, but, nevertheless, traces of uncombined hydrochloric or hydrobromic gas are found after the experiment, showing the temporary decomposition which the hydrochlorate or hydrobromate has undergone. If, during the cooling, the amylene does not again wholly combine with the acid set free at a high temperature, it is because these bodies, when cold, have not sufficient affinity to become entirely saturated, as took place with the elements of chloride of ammonium.

Finally, M. Wurtz has recently shown that heat is disengaged when a current of amylene and a current of hydrobromic acid are passed into a globe which is heated to a temperature at which the hydrobromate of amylene, without being completely separated, has, notwithstanding, a considerable tendency to separation.

These beautiful experiments of M. Wurtz show the true interpretation which ought to be given to M. Deville's works, and decide the question in favour of Ampère's hypothesis. Whatever the theory may be, it is nevertheless true that, in practice, errors would be committed by trusting exclusively to vapour densities in order to determine molecular weights. Whether or not it is due to separation, these densities may lead us into error, and proper means are necessary to enable us to verify the molecular weights with which they furnish us.

There is a compound of hydrogen and carbon (marsh gas) which has such a density that its molecular weight, deduced from this density, is equal to 16; is this weight exact?

Analysis shows us that marsh gas contains $\frac{3}{4}$ of its weight of carbon and $\frac{1}{4}$ of hydrogen; if, therefore, its molecular weight be 16, this weight is formed of 12 parts of carbon corresponding to 1 or more atoms of this body,* and of 4 parts of hydrogen equalling 4 atoms, as the atom of hydrogen weighs 1.

An atom being a mass indivisible by chemical agents, the smallest quantity of hydrogen which, in the compound in question, can be replaced by another body is equal to 1, that is to say, to the fourth part of the hydrogen contained in the substance; if therefore the molecular weight of marsh gas is in reality 16, for $\frac{1}{4}$, or for $\frac{2}{4}$, or for $\frac{3}{4}$, or for $\frac{4}{4}$, of the hydrogen, another simple body could be substituted.

If, on the contrary, the molecular weights of marsh gas were only 8, this gas would be composed of 6 of carbon and 2 of hydrogen. Then only the half or the whole of this latter element could be replaced by another; never the fourth part. Finally, if the molecular weight were 32, there would be 8 of hydrogen, and this metalloid could be replaced by eighths.

In marsh gas hydrogen can be replaced by fourths, and only by fourths; its molecular weight deduced from its vapour density is therefore correct. To recapitulate, the vapour densities in most cases give the molecular weights correctly; but as there exist several exceptions we must always check the results deduced by the system of substitutions.

**Atomic Weights.**—Two methods are used for the determination of atomic weights. One is founded on the fact that atoms represent the smallest quantity of a body that can enter into reaction; the other is based upon specific heats. These two methods are both indispensable, because they cannot always be employed indiscriminately. When they can both be employed they are a mutual help in checking each other.

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* I say one or more, because I do not suppose the atomic weight of carbon to be known.

First Method.—To determine the atomic weight of a simple body, we must first know its molecular weight in a free state and that of all the compounds, or at least the greater number of compounds, which it forms; and we must also know the quantitative composition of these latter. We then take, as the weight of the atom, the greatest number which divides exactly the weights of the body contained either in its free molecule or in that of its different compounds. A molecule can only contain a number of entire atoms, because these are indivisible; and the weight of any number of atoms is necessarily always capable of being divided by that of one atom. An example is necessary to understand clearly the preceding, and as we wish to justify the assertion we made relative to hydrogen—that its molecule contains two atoms—we will commence by determining the atomic weight of this element.

On comparing the weights of equal volumes of free hydrogen, hydrochloric acid, hydrobromic, hydriodic, hydrocyanic, hydro-sulphuric, hydroselenic, and hydrotelluric acids, ammonia, phosphoretted hydrogen, arseniuretted hydrogen, ethylene, propionic acid; vapours of alcohol, ether, acetic acid, formic acid and water; we find for the molecules of these different bodies weights which, compared to that of the molecule of hydrogen taken as unity (and not to that of the atom which we suppose to be as yet unknown), are as follows:

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| Names of Bodies. | Weight of their Molecules, taking the Molecule of H = 1. | Quantitative composition of the Molecule. | |
|---|---|---|---|
| | | Quantity of H contained in the Molecule. | Quantities of other Bodies contained. |
| Hydrogen (free) | 1 | 1 | |
| Hydrochloric acid | 18·25 | $\frac{1}{2}$ | 17·75 of chlorine. |
| Hydrobromic acid | 40·50 | $\frac{1}{2}$ | 40 of bromine. |
| Hydriodic acid | 64 | $\frac{1}{2}$ | 63·5 of iodine. |
| Hydrocyanic acid | 13·5 | $\frac{1}{2}$ | 13 of carbon and nitrogen (united). |
| Water | 9 | 1 | 8 of oxygen. |
| Hydrosulphuric acid | 17 | 1 | 16 of sulphur. |
| Hydroselenic acid | 40·75 | 1 | 39·75 of selenium. |
| Hydrotelluric acid | 65·5 | 1 | 64·5 of tellurium. |
| Formic acid | 23 | 1 | 22 of carbon and oxygen (united). |
| Ammonia | 8·5 | $1\frac{1}{2}$ | 7 of nitrogen. |
| Phosphoretted hydrogen | 17 | $1\frac{1}{2}$ | 15·5 of phosphorus. |
| Arseniuretted hydrogen | 39 | $1\frac{1}{2}$ | 37·5 of arsenic. |
| Acetic acid | 30 | 2 | 28 of carbon and oxygen (united). |
| Ethylene | 14 | 2 | 12 of carbon. |
| Propionic acid | 37 | 3 | 34 of carbon and oxygen (united). |
| Alcohol | 31 | 3 | 28 of carbon and oxygen (united). |
| Ether | 37 | 5 | 32 of carbon and oxygen (united). |

We see, on examining this table, that the greatest common divisor of the numbers $\frac{1}{2}$, 1, $\frac{3}{2}$, 2, 3, 5, which express the weights of hydrogen contained in the molecules of the different bodies examined, is $\frac{1}{2}$; $\frac{1}{2}$ represents therefore the weight of the atom of this body. All the weights used in this table have reference to the molecule of hydrogen;

to say that hydrogen has an atom which weighs $\frac{1}{2}$ is to say that its atom weighs only half as much as its molecule.

If we take as unity the weight of this atom instead of the molecule, this latter becomes equal to 2, and all the numbers which appear in the preceding table will be doubled. It will then take the following form:

| Names of Bodies. | Molecular Weights taken relatively to the atom of Hydrogen. | Quantitative composition of the Molecule. | |
|---|---|---|---|
| | | Quantity of H contained in the Molecule. | Quantities of other Bodies contained. |
| Hydrogen (free) | 2 | 2 | |
| Hydrochloric acid | 36·5 | 1 | 35·5 of chlorine. |
| Hydrobromic acid | 81 | 1 | 80 of bromine. |
| Hydriodic acid | 128 | 1 | 127 of iodine. |
| Hydrocyanic acid | 27 | 1 | 26 of cyanogen. |
| Water | 18 | 2 | 16 of oxygen. |
| Hydrosulphuric acid | 34 | 2 | 32 of sulphur. |
| Hydroselenic acid | 81·50 | 2 | 79·50 of selenium. |
| Hydrotelluric acid | 131 | 2 | 129 of tellurium. |
| Formic acid | 46 | 2 | 44 of carbon and oxygen. |
| Ammonia | 17 | 3 | 14 of nitrogen. |
| Phosphoretted hydrogen | 34 | 3 | 31 of phosphorus. |
| Arseniuretted hydrogen | 78 | 3 | 75 of arsenic. |
| Acetic acid | 60 | 4 | 56 of carbon and oxygen. |
| Ethylene | 28 | 4 | 24 of carbon. |
| Propionic acid | 74 | 6 | 68 of carbon and oxygen. |
| Alcohol | 62 | 6 | 56 of carbon and oxygen. |
| Ether | 74 | 10 | 64 of carbon and oxygen. |

Now that we have established our theory that a molecule of hydrogen is composed of two atoms, we will seek by the same process to determine the atomic weight of nitrogen; but according to custom we bring all the molecular weights to the weight of the atom of hydrogen, not to that of its molecule.

For this purpose we will, as before, examine the molecular weights and the composition of the different volatile compounds of nitrogen, such as protoxide and binoxide of nitrogen, hyponitric and hydrated and anhydrous nitric acids, and ammonia; we can thus form the following table:

| Names of Bodies. | Molecular Weights taken relatively to the atom of Hydrogen = 1. | Amount of Nitrogen contained in the Body. | Amount of other Bodies. |
|---|---|---|---|
| Protoxide of nitrogen | 44 | 28 | 16 of oxygen. |
| Binoxide of nitrogen | 30 | 14 | 16 of oxygen. |
| Hyponitric acid | 46 | 14 | 32 of oxygen. |
| Hydrated nitric acid | 63 | 14 | 49 of oxygen and hydrogen united. |
| Anhydrous nitric acid | 108 | 28 | 80 of oxygen. |
| Ammonia | 17 | 14 | 3 of hydrogen. |
| Nitrogen | 28 | 28 | |

We see that nitrogen enters into the molecule of the different bodies which appear in this table for a weight equal sometimes to 14, sometimes to 28. Fourteen being the greatest common divisor of these numbers, will represent the atomic weight of nitrogen. To falsify this conclusion it would be necessary to discover a new compound of nitrogen into the molecule of which would enter a quantity of this metalloid equal to a divisor of 14.

Second Method.—We owe this method to Dulong and Petit, who, knowing already the atomic weights of many bodies, saw that, to elevate 1 degree of heat, weights of different simple bodies proportional to their atomic weights, always required the same quantity of heat. Thus to elevate 1 degree 23 grammes of sodium, 32 grammes of sulphur, 118 grammes of tin, 31 grammes of phosphorus, etc., required the same quantity of heat—a quantity which we will represent provisionally by the letter P.

As we know that specific heat, or capacity for heat, is the quantity of heat necessary to elevate 1 degree the unity of weight of a body, let us see what is the specific heat of 4 elements, representing it by P.

P elevates 1 degree 23 grammes of sodium; thus it is evident that to elevate equally 1 degree 1 gramme, that is to say 23 times less of this element, 23 times less heat would be required, that is to say $\frac{P}{23}$; $\frac{P}{23}$ therefore represents the capacity of sodium for heat.

We find that the capacity for heat of sulphur is $\frac{P}{32}$, that of tin $\frac{P}{118}$, that of phosphorus $\frac{P}{31}$.

Thus we see that the specific heats decrease as the atomic weights augment, and that in the same proportion: if the atomic weights be 1, 2, 4, 8, 16, etc., the specific heats will be $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, $\frac{1}{16}$, etc.

Arithmetic teaches us that if the two factors of a multiplication undergo such modifications that one of them becomes 2, 3, 4, 5 times less, while the other becomes 2, 3, 4, 5 times more, the product is unchanged. We ought therefore always to obtain the same number when we multiply the specific heat of different bodies (which we find by the help of physical means) by the atomic weights of these same bodies.

Thus the product of the atomic weight of sodium multiplied by its specific heat will be $\frac{P \times 23}{23} = P$. The product of the atomic weight of sulphur by its specific heat will be $\frac{P \times 32}{32} = P$.

The constant number P has been determined numerically to be 6·666.

If we wish to know the atomic weight of a simple body; to determine its specific heat, let C be this heat, and $x$ its unknown atomic weight, we have:

$$C \times x = 6{\cdot}666\text{; thence we take } x = \frac{6{\cdot}666}{C}.$$

Thus we find the atomic weight by dividing the number 6·666 by the specific heat, the result of experience.

Dulong and Petit have expressed this law by saying that specific heats are inversely proportional to atomic weights.

In order to employ this method, the bodies must be in the same state when their specific heat is determined. Thus the specific heat of gases could not serve to determine their atomic weight; but in this case we arrive at the result sought for by a complicated method.

M. Vœstyn has shown that in compound bodies each atom retains its specific heat. If a compound body contains in its molecule 2, 3, or 4 simple atoms, the product of its specific heat by its molecular weight will be 2, 3, or 4 times the constant number 6·666.

If therefore we wish to ascertain the atomic weight of a gas, we engage it in a combination which can take the solid state, and of which we determine the specific heat; we multiply the number which represents this capacity for heat by the molecular weight of the compound, and by dividing the product by 6·666, we have for quotient the number of atoms which constitute the molecule. The analysis of the compound being made, and the atomic weight of one of its constituent elements being known, the atomic weight of the other is naturally deduced.

For example, if we wish to find by this means the atomic weight of oxygen, we combine it with hydrogen, and determine the specific heat of the water formed, or, rather, we know that it is equal to 1, because the specific heat of water has been taken as unity of specific heat. On the other hand, we determine the molecular weight of the water, and find it equal to 18.

Now, as 18 contains 3 times 6, we thence conclude that the water contains 3 atoms; and the analysis of the water being made, we find that 18 of water contain 16 of oxygen and 2 of hydrogen.

We know already that the weight of the atom of hydrogen is 1, and thence we conclude that the atom of oxygen weighs 16. If it weighed less than 16, there would be more than 1 in the molecule of water, and as this already contains 2 atoms of hydrogen, it would contain more than 3 atoms, which would be in contradiction to the deduced conclusions of the capacity of water for heat.

We have seen that instead of dividing 18 by 6·666, we only divided it by 6, because the number P is not absolutely constant, but varies between 6 and 7; in taking 6·666, we only took a mean, and this in no way invalidates the law nor the results deduced from it.

The specific heats are only approximately determined, because we cannot know the quantity of heat which a body absorbs to dilate at the same time that it becomes heated, a quantity which is in addition to the specific heat and falsifies the results; but this slight discrepancy between theory and experiment has no inconvenience; it tends, it is true, to give to atomic weights a little inexactness; but, fortunately, the approximation is near enough to allow the analysis of compounds into which the bodies enter whose atomic weights we seek, to determine completely these latter.

To ascertain the atomic weight of silver, we divide the number 6·666 by its specific heat 0·05701, and we thus obtain $\frac{6\cdot666}{0\cdot05701} = 117$; if, on the other side, we combine silver with chlorine and analyse the chloride of silver, we find that for 35·5 of chlorine this compound contains 108 of silver.

As 35·5 represents the weight of an atom of chlorine, we consider it as combined with 1, 2, 3, 4, etc., atoms of silver; and according to these different hypotheses, the atomic weight of silver will be 108, 54, 27, etc.

Or we can suppose in chloride of silver a single atom of silver for 2, 3, 4, 5, etc., atoms of chlorine, so that the quantity of silver combined with 35·5 of chlorine will only represent the half, the quarter, the fifth, etc., of the weight of its atom. Under these different hypotheses, the atomic weight of silver would be 216, 324, 432, 540, etc. We can still take other hypotheses; but whatever they may be, they all give for the atomic weight of silver numbers which are considerably distant from the number 117 found by specific heat. Only one supposition gives a value which at all accords with this number; it is that from which we deduce the atomic weight 108; 108 ought therefore to be considered as the true atomic weight of silver.*

We shall now state the atomic weights of the different simple bodies. As we have already remarked, these weights are not to be confounded with the old equivalents of which they often represent the multiples, but with which they have sometimes less simple relations; it is necessary also to place them in juxtaposition with these old equivalents, as elementary works still employ the latter. We give a table of four columns, of which the first contains the names of the elementary bodies; the second, the symbols by which they are ordinarily represented; the third, their atomic weights; and the fourth, their equivalents.

In this table we have marked with an asterisk the bodies which are of so little importance and so little known that they do not require a detailed description.

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* Three bodies, *boron*, *silicon*, and *carbon*, have atomic weights which do not correspond to those deduced from their specific heats. But these three bodies assume different allotropic states in each of which their specific heat varies. This exception does not disprove the law.

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| Names of the Elements. | Symbols which represent them. | Atomic Weights. | Equivalents. |
|---|---|---|---|
| Hydrogen | H | 1 | 1 |
| Chlorine | Cl | 35·5 | 35·5 |
| Bromine | Br | 80 | 80 |
| Iodine | I | 127 | 127 |
| Fluorine | F | 19 | 19 |
| Oxygen | O | 16 | 8 |
| Sulphur | S | 32 | 16 |
| Selenium | Se | 79·50 | 39·75 |
| Tellurium | Te | 129 | 64·5 |
| Boron | B | 11 | 11 |
| Carbon | C | 12 | 6 |
| Silicon | Si | 28 | 21 |
| Girconium* | Gr | 89·6 | 33·6 |
| Tin | Sn | 118 | 59 |
| Titanium* | Ti | 50 | 25 |
| Thorinum* | Th | 231·5 | 57·87 |
| Nitrogen | N | 14 | 14 |
| Phosphorus | P | 31 | 31 |
| Arsenic | As | 75 | 75 |
| Antimony | Sb | 122 | 122 or 61 |
| Bismuth | Bi | 210 | 155 |
| Potassium | K | 39 | 39 |
| Sodium | Na | 23 | 23 |
| Lithium* | Li | 7 | 7 |
| Cæsium* | Cs | 133·036 | 133·036 |
| Rubidium* | Rb | 85·36 | 85·36 |
| Thallium | Tha | 204 | 204 |
| Silver | Ag | 108 | 108 |
| Barium | Ba | 137 | 68·5 |
| Strontium | Sr | 87·5 | 43·75 |
| Calcium | Ca | 40 | 20 |
| Magnesium | Mg | 24 | 12 |
| Glucinium* | Gl | 14 | 7 |
| Yttrium | Yt | 64·30 | 32·18 |
| Erbium* | Erb | Unknown. | Unknown. |
| Terbium* | Ter | Unknown. | Unknown. |
| Cerium* | Ce | 92 | 46 |
| Lanthanum* | La | 92·8 | 46·4 |
| Didymium* | Di | 96 | 48 |
| Lead | Pb | 207 | 103·5 |
| Mercury | Hg | 200 | 100 |
| Copper | Cu | 63 | 31·5 |
| Zinc | Zn | 65 | 32·5 |
| Cadmium | Cd | 112 | 56 |
| Nickel | Ni | 59 | 29·5 |
| Cobalt | Co | 59 | 29·5 |
| Chromium | Cr | 53·5 | 26·75 |
| Manganese | Mn | 55 | 27·5 |
| Iron | Fe | 56 | 28 |
| Molybdenum | Mo | 96 | 48 |
| Tungsten | W | 184 | 92 |
| Vanadium | V | 68·5 | 68·5 |
| Uranium* | U | 120 | 60 |
| Aluminum | Al | 27·5 | 13·75 |
| Niobium* | Nb | 94 | † |
| Pelopium* | Pe | Unknown. | Unknown. |
| Tantalum* | Ta | 230 | 92† |

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† The atomic weights of tantalum and niobium have just now been modified by M. Marignac.

| NAMES OF THE ELEMENTS. | Symbols which represent them. | Atomic Weights. | Equivalents. |
|---|---|---|---|
| Gold | Au | 196·5 | 98·25 |
| Platinum | Pt | 197 | 98·5 |
| Osmium* | Os | 197 | 98·5 |
| Iridium* | Ir | 197 | 98·5 |
| Rhodium* | Rh | 104 | 52 |
| Palladium* | Pd | 106·5 | 53·25 |
| Ruthenium* | Ru | 104 | 52 |
| Indium* | In | Unknown. | 35·919 |

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## NOTATION, FORMULAS, AND CHEMICAL EQUATIONS.

Chemical notation has for its object the representation of all known bodies by abridged formulas, which indicate at once their molecular weight, their qualitative and their quantitative composition; they enable the signification of the different reactions to be more readily comprehended.

To construct these formulas a symbol is used which represents the atom (not the molecule) of each simple body; these are the symbols which we have placed on the preceding table. These symbols are usually obtained by taking the first letter of the name of the body; thus O for oxygen, S for sulphur, etc.† When there are several bodies whose names commence with the same letter, the first letter is reserved to designate the oldest known amongst them, and for the symbols of the others the first two letters of their names are used. Thus sulphur, selenium, strontium, silicon, all commence with S; S signifies sulphur, while we take Si for silicon, Se for selenium, and St for strontium.

There are, nevertheless, several exceptions to this rule: sometimes, instead of the first two letters, we take the first and one of those in the body of the word. Thus, arsenic is As, stannum (tin) Sn, stibium (antimony) Sb, hydrargyrum (mercury) Hg.

Several symbols are taken from the Latin, as the last three; some are from the German. The symbol of tungsten is W, from the German Wolfram.

All simple bodies being indicated by a symbol, nothing is easier than to represent a compound molecule. We have merely to write the symbols of the different constituent elements side by side, and to place above each an exponent figure which indicates the number of its atoms present. This exponent is dispensed with when the atom is single;

† Some symbols are employed barred, to indicate that they are taken with the value they have in atomic notation, and merely to avoid the confusion which might arise, as several authors still use the notation of equivalents.[1]

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[1] As, however, the latter notation is becoming disused, I have not thought it necessary to continue the use of the bars. *See* Preface.—(Tr.)

thus $SO^3$ represents a compound molecule formed of 1 atom of sulphur and 3 atoms of oxygen.

In writing by symbols it has been agreed to place first, that one of the different components which is the most electro-positive; but this rule is only followed exactly when there are not more than two elements present.

It is clear that the formulas of which we speak represent the qualitative composition of bodies; it is also clear that they represent their molecular weight. A molecule can have no other weight than the sum of the weight of the atoms forming it; therefore, in order to know how much it weighs, we have only to multiply the atomic weight of each element by its exponent and to add the products. Thus, glycerine having as its formula $C^3H^8O^3$, its molecular weight will be equal

| | |
|---|---|
| to the weight of 3 atoms of carbon . . | $3 \times 12 = 36$ |
| + the weight of 8 atoms of hydrogen . | $8 \times 1 = 8$ |
| + the weight of 3 atoms of oxygen . . | $3 \times 16 = 48$ |
| Total . . . . . . . . | 92 |

These formulas also represent the centesimal composition of bodies. Knowing the quantity of the different elements contained in a certain weight of the compound which is that of its molecule, the knowledge of its centesimal composition is arrived at by simple proportion.

For example, to find the centesimal composition of acetic acid $C^2H^4O^2$, we should first deduce from this formula that the molecule of this acid weighs 60, and contains 2 atoms = 24 of carbon, 4 atoms = 4 of hydrogen, and 2 atoms, or 32 of oxygen.

Then we place the three proportions—

1st.—$60 : 24 :: 100 : x$, therefore $x = \frac{24 \times 100}{60} = \frac{24 \times 10}{6} = 40$

2nd.—$60 : 4 :: 100 : x$, therefore $x = \frac{4 \times 100}{60} = \frac{4 \times 10}{6} = 6{\cdot}666$

3rd.—$60 : 32 :: 100 : x$, therefore $x = \frac{32 \times 100}{60} = \frac{32 \times 10}{6} = 53{\cdot}333$

Now we understand how by the help of a formula we can know the quantitative and qualitative composition, and the molecular weight of the compound which it represents. It remains for us to see, how a body being given, we can establish the formula: this is the other side of the problem.

To establish the formula of a compound body, we first seek by analysis what is its centesimal composition; then we determine its molecular weight. By a series of proportions we then seek the composition of a weight of this substance which we have agreed to represent as the weight of its molecule. Then we divide the quantities of its different elements by their atomic weights; the quotient shows how many atoms of each it contains. It then suffices to write side by side, commencing with the most electro-positive, the symbols which express the different atoms, and to place above these symbols an exponent which indicates the numbers of these atoms.

Let us apply this rule to a particular example: to establish the formula of *propionic* acid. We analyze this acid, and see that it contains n a hundred parts 48·648 of carbon, 43·243 of oxygen, and 8·108 of hydrogen (these figures added give 99·999, say 100).

Then we will seek its molecular weight, which we find equal to 74.

This done, we place the three proportions—

1st.—100 : 48·648 :: 74 : $x$, therefore $x =$ 35·999, say 36
2nd.—100 : 43·243 :: 74 : $x$, therefore $x =$ 31·999, say 32
3rd.—100 : 8·108 :: 74 : $x$, therefore $x =$ 5·999, say 6

Thus a molecule of propionic acid weighs 74, and contains 36 of carbon, 6 of hydrogen, and 32 of oxygen. The atom of carbon weighing 12, we shall have the number of atoms of this body contained in the molecule of propionic acid on dividing by 12 the weight which it contains; that is to say, 36; and as $\frac{36}{12} = 3$, we conclude that it contains 3 atoms of carbon.

Also, the atom of oxygen weighing 16, we will divide by 16 the weight of oxygen which the molecule contains: $\frac{32}{16} = 2$, propionic acid thus contains 2 atoms of oxygen.

Lastly, the atom of hydrogen weighs 1, and as there are 6 of hydrogen, we conclude that propionic acid contains 6 atoms of this element, as $\frac{6}{1} = 6$.

The formula of propionic acid will, therefore, be $C^3H^6O^2$.

Sometimes it is necessary to indicate that a certain number of molecules of the same body take part in a reaction. Then we place to the left of the formula a coefficient indicating this number. It is thus that to express 3 molecules of propionic acid we write $3C^3H^6O^2$.

Thus, to understand reactions precisely, it is usual to represent them by equations. In these equations the first member contains the formulas of the different bodies which enter into the reaction, preceded by the coefficient which indicated how many molecules are present; and the second member, which is separated from the first by the sign =, contains the formulas of the products which are formed after the reaction. As nothing is lost in chemical actions, it is clear that the second member of the equation ought to contain exactly all the atoms which existed in the first, differently grouped.

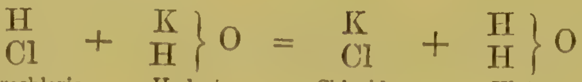
For example, take the reaction which occurs in the formation of chloride of potassium KCl from hydrochloric acid HCl, and potash KHO.

| | | | | | | |
|---|---|---|---|---|---|---|
| $KHO$ | + | $HCl$ | = | $KCl$ | + | $H^2O$ |
| Potash. | | Hydrochloric acid. | | Chloride of potassium. | | Water. |

The atom of potassium, the two atoms of hydrogen, the atom of oxygen, and the atom of chlorine which form the first member, reappear in the second, only they are grouped differently.

## RADICLES, ATOMICITY OF RADICLES.

In chemistry, under the name of radicle, is designated each atom or group of atoms, capable either of being transferred from one compound to another by means of double decomposition, or of existing in a free state and entering directly into combination. If the radicle is constituted of a simple atom it is called a simple radicle; if it is constituted by groups of atoms it is called a compound radicle. In short, the term simple radicle is synonymous with atom, and the term compound radicle indicates a group of atoms acting the same part as a simple atom. The following formulas enable us to get a clear idea of what is meant by radicles:



$$\underset{\text{Hydrochloric acid.}}{\begin{matrix}H\\Cl\end{matrix}} + \underset{\text{Hydrate of potash.}}{\left.\begin{matrix}K\\H\end{matrix}\right\}O} = \underset{\text{Chloride of potassium.}}{\begin{matrix}K\\Cl\end{matrix}} + \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O}$$

The atoms H, Cl, and K, are simple radicles, because each only contains one atom, and can be transferred from one compound to another by means of double decomposition. But the residue HO of the molecule of potash being likewise transferred in the same manner, ought to be called a compound radicle, though it is not capable of isolation. The following example shows a compound radicle capable of isolation:

$$\underset{\text{Ethylene.}}{C^2H^4} + \underset{\text{Chlorine.}}{2Cl} = \underset{\text{Chloride of ethyl.}}{C^2H^4Cl^2}$$

As ethylene is capable of combining directly with chlorine, like simple bodies, it ought to be considered a compound radicle.

The first property to be regarded in a simple or compound radicle is its capacity for saturation.

We will first consider it in simple radicles; and, to avoid confusion, we will use the word atom. We have seen that the equivalent of oxygen, that is to say, the ponderable quantity of this body which is substituted for 1 of hydrogen, or which combines with it, is equal to 8, and that the atom of oxygen weighs 16, that of hydrogen weighing 1; that is to say, that 1 atom of oxygen can take the place of, or can combine with, 2 atoms of hydrogen.

We have also seen that the equivalent of chlorine, like its atomic weight, is 35·5, which shows us that the atom of chlorine only combines with, or is only substituted for, a single atom of hydrogen.

From the preceding facts, we deduce that an atom of chlorine requires only half as much hydrogen to saturate it as does an atom of oxygen; and to explain this, we will say that chlorine is monatomic, and that oxygen is biatomic.

Similar considerations show us that 1 atom of boron can combine

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with 3 atoms of chlorine; that is to say, with 3 atoms of a monatomic body: that 1 atom of carbon can combine with 4 atoms of hydrogen or chlorine; and that one atom of phosphorus can combine with 5 atoms of chlorine; we thence conclude that boron is triatomic, carbon tetratomic, and phosphorus pentatomic.

To sum up, we call monatomic the atoms and radicles which combine with 1 of hydrogen or take its place; biatomic, those which combine with 2 atoms either of hydrogen or of another monatomic body, or which take the place of 2 atoms of these bodies; we call triatomic those which combine with, or take the place of 3 atoms of hydrogen or any other monatomic body, and so on.

It will have been noticed that we always say radicles capable of combining with *n* atoms of hydrogen or of taking the place of *n* atoms; that is, in effect, that they may be combined with an atom, or be substituted for an atom in a like manner.

Every stable body may be considered as a molecular edifice in equilibrium. In a molecule, each atom represents a force, therefore it is necessary for equilibrium that the resultant of the forces proceeding from all the other atoms be equal and contrary to it. If we take the molecule of alcohol $C^2H^6O$, we can only conceive its atoms being in equilibrium when the force represented by one of the 9 which constitutes it is exactly balanced by the resultant of the forces represented by the other 8. Thus $C^2H^6$ ought to represent the same force as O, $C^2H^5O$ the same force as H, C the same force as $CH^6O$, etc.

This point once established, it is evident that to substitute 1 atom of chlorine, say, for 1 atom of hydrogen, is to combine this atom of chlorine with the atomic group which formerly was united to the hydrogen, and was capable of maintaining it in equilibrium, and which has consequently the same value as 1 atom of free hydrogen.

To find the atomicity or capacity for saturation of simple bodies, we determine the atomic weight of these bodies, and then combine them with the greatest possible quantity either of hydrogen or of another body of the same atomicity (chlorine, bromine, iodine, etc). Thus we see with how many of these monatomic radicles the atom of the simple body in question is capable of combining. This number represents its atomicity.

Let us, for example, find the atomicity of carbon. After having determined its atomic weight, we study its different compounds with hydrogen, and find that the formula of the one in which an atom of carbon C is joined to the greatest quantity of hydrogen is $CH^4$. We thence conclude that carbon is tetratomic. The atomicity of a simple body represents, therefore, the maximum quantity of a monatomic radicle which can be combined with that body. Nevertheless, it must not be thought that a polyatomic body can make no other combinations than those which correspond to its maximum atomicity. Far from this, it can generally make all the combinations, or, at least, a great number of the combinations less saturated than is in accordance with the theory. Thus, in considering a tetratomic combination of a radicle R, $R^{iv}H^4$, we may say that the combinations $R^{iv}H^3$, $R^{iv}H^2$, $R^{iv}H$ are generally possible. This is the case with tin. This metalloid is capable of combining with 4 times the monatomic compound radicle $C^2H^5$, producing the body $Sn^{iv}(C^2H^5)^4$; but beside this combination, tin also gives the compounds $Sn^{iv}(C^2H^5)^3$, $Sn^{iv}(C^2H^5)^2$.

Many chemists explain the preceding fact by saying that one body has several atomicities. I prefer to keep the word atomicity to indicate only the maximum capacity for saturation of a body, and to consider all those of its compounds which have an inferior degree of combination as non-saturated, or incomplete molecules.

Nevertheless, as it is also useful to have a word to express the actual value of substitution of an atom or of a compound radicle, we will use M. Hofmann's designation of this property, "quantivalence," and speak of "monovalent radicles," "bivalents," etc.

Thus we say that lead, whose atomicity is equal to four, is only bivalent in the greater part of its combinations.

In notation we express this quantivalence, the capacity for saturation of radicles, by placing over the symbols which represent them a certain number of dashes; but when more than three dashes would be required it is preferable, to render the reading easier, to use Roman figures, IV. V. VI., etc. When the radicle is monatomic no sign is used; thus—

$$Cl \qquad O'' \qquad Bo''' \qquad C^{IV} \qquad P^{V}$$

signify that chlorine is monovalent, oxygen bivalent, boron trivalent, etc.

It is important to remark that the apostrophes or Roman figures mark the actual value of substitution—the quantivalence of a radicle, and not its atomicity. The atomicity being an absolute invariable value, it is useless to mark it, it is known once for all. The quantivalent, on the contrary, varying according to the compounds into which a radicle enters, ought to be carefully indicated.

The invariability of the atomicity of simple bodies enables us to comprehend compound radicles. These latter are only incomplete non-saturated molecules.

Thus carbon C, being saturated when it is in the state of marsh gas $CH^4$, can, nevertheless, combine with 1, 2, or 3 molecules of hydrogen; but then the molecules which result are incomplete, and tend to become complete by taking as much hydrogen, or any other body of which they are in need, in order to pass to the complete state $Cx^4$: it follows that $CH^3$ can only take one monatomic atom; it will, therefore, be a monatomic radicle. $CH^2$ can take 2 monatomic atoms, or 1 diatomic atom, to become complete; it will be a biatomic radicle. Lastly, CH can take 3 monatomic atoms, or 1 triatomic atom, to become complete; this will be a triatomic radicle.

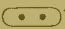
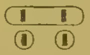
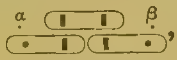
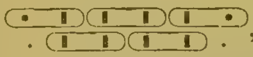
The three radicles below do not exist in a free state, but they may be considered as forming part of certain compounds. Thus we may admit that the radicle

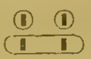
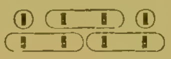
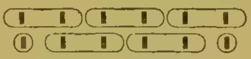
$CH^3$ exists in chloride of methyl $\left.\begin{matrix}CH^3\\Cl\end{matrix}\right\}$

$CH^2$ „ iodide of methylene $\left.\begin{matrix}CH^{2\prime\prime}\\I^2\end{matrix}\right\}$

$CH$ „ in chloroform $\left.\begin{matrix}CH^{\prime\prime\prime}\\Cl^3\end{matrix}\right\}$

As we see by these examples, it is by their combinations with monatomic bodies that we determine the atomicity of compound radicles. We could not deduce the capacity for saturation of any radicle from the combinations which it forms with polyatomic radicles. These have the property of accumulating indefinitely in the molecules. M. Kékulé has given a hypothetical, but very elegant and probable explanation of this.

For example, let us take a biatomic atom. M. Kékulé represents it by the symbol *, which indicates two distinct centres of attraction. It is clear that if to each of these centres a monatomic atom is adapted, the biatomic atom will be saturated and incapable of combining with any other body whatever; the resultant molecule will have the form ; but if this atom is combined by each of its centres of attraction with one of the centres of attraction of another atom, like it biatomic, the molecule takes the form , where we see there remain at $\alpha$ and $\beta$ two non-saturated centres of attraction. Then we could have successively the chain , and others still more complicated, until two monatomic atoms should come to close the molecule by giving it the form

 or  or 

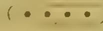
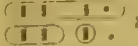
The combinations with polyatomic radicles give no indication of atomicity, and to determine it we must always have recourse to combinations with monatomic radicles.

Experience has proved that simple radicles or monatomic compounds never exist in a free state without being doubled; that is to say, without having a molecule formed of 2 atoms, or of 2 of the atomic groups which take their place.

Thus the radicles H, Cl, Br., etc., in a free state, exist in the forms

$\left.\begin{matrix}H\\H\end{matrix}\right\}$ $\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}$ $\left.\begin{matrix}Br\\Br\end{matrix}\right\}$

---

* In these figures the circles or the ellipses represent atoms and the points or the lines placed inside represent their centres of attraction. When the atoms are placed side by side, the lines which are made opposite indicate affinities which saturate each other. Simple points placed outside the atoms opposite the internal points of these latter indicate affinities not saturated. Thus  means a tetratomic atom, and  signifies a tetratomic atom with three affinities saturated; two by a diatomic atom, and one by a monatomic atom; the fourth remaining free.

and only in these forms. There is, however, an exception to this rule, hyponitrous acid, whose formula is $NO^2$, and not $\left.\begin{matrix}NO^2\\NO^2\end{matrix}\right\}$.

Biatomic radicles can exist in a free state with a molecule formed of 2 atoms, as well as with a molecule formed of only one.

It is thus that the radicles O, S, Se, Te have molecules represented by the symbols—

$$\left.\begin{matrix}O''\\O''\end{matrix}\right\}\qquad\left.\begin{matrix}S''\\S''\end{matrix}\right\}\qquad\left.\begin{matrix}Se''\\Se''\end{matrix}\right\}\qquad\left.\begin{matrix}Te''\\Te''\end{matrix}\right\}$$

while the symbols $Hg''$, $Cd''$, $C^2H^{4''}$, $C^3H^{6''}$ represent both the atom and the molecule of mercury, cadmium, ethylene, and propylene. The only known simple triatomic radicles are boron, thallium, gold and vanadium; and the only known compound triatomic radicles are allyl $\left.\begin{matrix}C^3H^{5'''}\\C^3H^{5'''}\end{matrix}\right\}$, the binoxide of nitrogen NO, and kakodyl $\left.\begin{matrix}(CH^3)^2As'''\\(CH^3)^2As'''\end{matrix}\right\}$. We know nothing of the constitution of the molecule of boron or thallium, gold or vanadium, whose vapour densities chemists have not yet succeeded in taking. As to allyl and kakodyl, their molecule is double; but, on the other hand, that of binoxide of nitrogen is simple.

The known tetratomic radicles of which the density in the gaseous state has been ascertained have an atom which is the same as the molecule.

Among the known pentatomic radicles, some have a molecule formed of 2 atoms like nitrogen, and others have a molecule formed of 4 atoms like phosphorus and arsenic.

Lastly, the only hexatomic radicle which we have in a free state, benzine $(C^6H^6)^{vi}$, has a formula which corresponds both with the free molecule of this body and with the radicle as it enters into combinations.

From all these facts, we gather that if the radicles of uneven atomicity have a tendency to have a double molecule when in a free state, certain of them nevertheless can have a simple, and others a quadruple molecule.

M. Delavaud, starting from the idea that radicles of uneven atomicity can never exist in a free state without becoming doubled, has propounded a theory which had already been started by M. Erlenmeyer, who, however, had not deduced from it such interesting consequences; M. Delavaud thought that this theory accounted for the non-existence of radicles of uneven atomicity in a free state, and even the fact of the atomicity; it may be summed up in two propositions:—

1st. No non-saturated molecule can exist in a free state.

2nd. Every polyatomic atom results from the union of a certain number of monatomic sub-atoms capable either of saturating each other or of being saturated by other radicles. Thus the atom of phosphorus $P^v$ would be formed of five sub-atoms, and we should have $P^v = (p'p'p'p'p')$. This being admitted, it is easy to explain that a radicle may have several quantivalences which may differ by an even number of units, as 2, 4, 6, etc.; hexatomic atoms may be hexavalent, tetravalent, bivalent, or neutral; and pentatomic atoms may be pentavalent, trivalent, or monovalent.

Let us take the atom of carbon $C^{IV} = (cccc)$. If the four sub-atoms are saturated by 4 strange radicles we should have $\left(\overset{1}{c}\,\overset{1}{c}\,\overset{1}{c}\,\overset{1}{c}\right)$ and the carbon $C^{IV}$ would act with its maximum atomicity.

But while two C are saturated by strange radicles it may be supposed that the other two saturate each other, giving biatomic carbon $C'' = \left(c - - c\,\overset{1}{c}\,\overset{1}{c}\right)$. Lastly, if the 4 sub-atoms saturate each other, we have free carbon $C^{0} = (c - - cc - - c)$. Carbon has, therefore, an absolute atomicity equal to the number of sub-atoms which its chemical atom contains; that is to say, to 4; it can, moreover, be bivalent or neutral.

Let us now take nitrogen; its absolute atomicity is equal to five: its chemical atom contains five sub-atoms. Further, it may act with the quantivalences 5, 3, 1, but it never can be neutral. It requires two sub-atoms for a reciprocal saturation, and, as the number of these sub-atoms is uneven, there always remains at least one that is non-saturated.

$$\begin{aligned} N^{v} &= (\overset{1}{n}\quad \overset{1}{n}\quad \overset{1}{n}\quad \overset{1}{n}\quad \overset{1}{n}) \\ N''' &= (n\ -\ -\ n\quad \overset{1}{n}\quad \overset{1}{n}\quad \overset{1}{n}) \\ N' &= (n\ -\ -\ n\quad n\ -\ -\ n\quad \overset{1}{n}) \end{aligned}$$

If, therefore, no non-saturated molecule can exist, the atom of nitrogen, such as we obtain in a free state, can never form a molecule, and the molecule of free nitrogen will always contain at least 2 atoms, in order that the 2 sub-atoms that have remained non-saturated in these latter may saturate each other. The molecule of free nitrogen then becomes—

$$\left.\begin{matrix} N \\ N \end{matrix}\right\} = \left(\left.\begin{array}{ccccccccccc} n & - & - & n & n & - & - & n & n \\ & & & & & & & & | \\ n & - & - & n & n & - & - & n & n \end{array}\right\}\right)$$

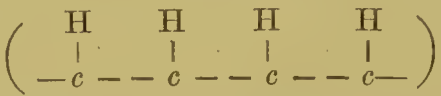
M. Delavaud's theory is ingenious, but it presents several difficulties.

In the first place, we do not see how the sub-atoms of which this chemist speaks remain together. Thus, in carbide of hydrogen,

$$CH^{4} = \left(\begin{array}{cccc} H & H & H & H \\ | & | & | & | \\ c & c & c & c \end{array}\right)$$

the four sub-atoms are held together by nothing.

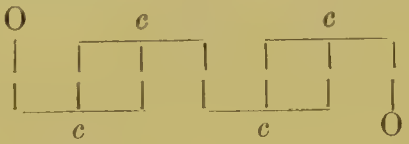
This difficulty may, nevertheless, be eluded by admitting that the sub-atoms of which we speak are all not mono, but triatomic, and by not seeking to explain this triatomicity, without which we should go from theory to theory for ever. In this case each sub-atom would exchange two affinities with its neighbour, and there would remain one free; the hydro-carbon $CH^4$ would then be—



$$\left(\begin{array}{cccc} H & H & H & H \\ | & | & | & | \\ -c-- & -c-- & -c-- & -c- \end{array}\right)$$

The triatomicity of the most simple radicles and the absence of any monatomic radicle would well accord with the triatomicity of iodine and the probable triatomicity of the other halogen bodies.

The variability of the quantivalence of a body would also be equally well explained by this triatomicity of the sub-atoms. Let it be, for example, oxide of carbon, we should have—



$= (c\,c\,c\,c\,o\,o) = CO.$

Unfortunately, there is a fact which overthrows M. Delavaud's theory; this is the existence of binoxide of nitrogen NO. According to this theory the radicle can only have an uneven atomicity. In effect, if there are two atoms, one of even, the other of uneven atomicity, in whatever way they may be united, the product would always have an uneven atomicity. On the other hand, it is impossible to doubt that the formula NO represents the real molecule of the binoxide of nitrogen. No dissociation can be admitted, because the body in question is gaseous. Such an exception completely overthrows this theory.

M. Delavaud's theory has another inconvenience which, even without the exception just spoken of, would prevent its adoption. It goes beyond the hypotheses permitted in experimental sciences; it is metaphysical. In the experimental sciences theories ought only to be the generalization or systemization of facts, which they ought never to exceed. M. Delavaud's theory exceeds facts, since it supposes sub-atoms, whose existence is not demonstrated. If such theories were allowed, a thousand might be propounded which would be as justifiable as that of M. Delavaud, and which would reciprocally oppose one another. Instead of confining ourselves within the limits of experiment, we should arrive at empty reasoning, like the metaphysicians of the Middle Ages.

For our part, as we do not wish to go beyond facts, we will admit that non-saturated molecules exist in a free state, because the oxide of carbon and many other bodies furnish proofs of it; and we shall also say that radicles of uneven atomicity can exist without becoming doubled, because this takes place with binoxide of nitrogen NO and hyponitrous acid $NO^2$.

This leads us to examine an idea of M. Wurtz, who sees an anomaly in the fact that the molecules of arsenic and phosphorus are $P^4$ and $As^4$, instead of $P^2$ and $As^2$, and that the molecules of biatomic metals are $Hg''$, $Zn''$, $Cd''$, instead of $Hg^2$, $Zn^2$, $Cd^2$.

This objection does not seem to be well grounded. Ampère's law does not say that for an equal volume all gases contain the same number of atoms, but only that they contain the same number of molecules. If it were otherwise, it would be necessary to establish a difference, which nothing would justify, between simple and compound bodies. In these latter the number of atoms varies greatly in different bodies, even though the gaseous volume occupied by the molecule remain the same. The molecular weights are given by the law of Ampère, but this law gives no indications of atomic weights; that is to say, of the number of atoms which the molecule contains. This number may be 1, 2, 4, etc., and may even vary in the same body, as the phenomena of allotropy prove. (*See* Allotropy.)

Is there any anomaly in the following fact, that bodies resembling each other like nitrogen and phosphorus have not similarly constituted molecules? We think not. Analogy and resemblance are not identity; and because two bodies give rise to many similar compounds it must not thence be concluded that the two series ought always to be identical. Were it otherwise than in the case of atoms of even atomicity, we do not see why mercury should be anomalous rather than oxygen. If there were any anomaly it would rather be on the side of the oxygen, since, with the exception of this body and its three congeners, all known radicles of even atomicity have a simple molecule.

We think the molecules of simple bodies are in all points analogous to those of compound bodies, and, like these latter, may contain, according to the case, a very variable number of atoms. The molecule of phosphorus $P^4$ and the molecule of mercury Hg are no more anomalies than the molecules $OH^2$ or $SeCl^4$.

SCHOOL OF MEDICINE

## MOLECULAR TYPES.

Thirty years ago, M. Dumas, generalizing the facts hitherto known relating to the action which chlorine and bromine exercise on organic substances, for the first time applied the idea of type to chemistry.

A compound in his eyes constituted a molecular type, in which one or more atoms of one body could be replaced by one or more atoms of another without the type being altered. Thus—

| | |
|---|---|
| Acetic acid | $C^2H^4O^2$, |
| Chloracetic acid | $C^2H^3ClO^2$, |
| Bichloracetic acid | $C^2H^2Cl^2O^2$, |
| And trichloracetic acid | $C^2H\ Cl^3O^2$, |

belonged, according to M. Dumas, to the same type, though in the three last the hydrogen of the acetic acid was partially replaced by chlorine.

Laurent, following the same idea, asserted what has since been proved to be incorrect. He said that bodies derived by substitution were always allied by the closest analogy of properties to those from which they were derived.

Later still, Dr. Williamson remarked that alcohol $C^2H^6O$, already regarded as an hydrate of the radicle ethyl $C^2H^5$, may be considered as being derived from a molecule of water by the substitution of ethyl for the half of the hydrogen :—

$$\begin{array}{ccc} \left.\begin{matrix}H\\H\end{matrix}\right\}O & \qquad\qquad & \left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O \\ \text{Water.} & & \text{Alcohol.} \end{array}$$

The idea of type thus advanced a step. In order to class two bodies in one type it was no longer necessary for them to resemble each other in their properties ; it was sufficient if they were capable of undergoing analogous metamorphoses.

Finally, Gerhardt, generalizing this view, classed side by side bodies having very different properties; so that a chemical type becomes nothing more than a general system of reactions. Acetic acid, water, and alcohol, are classed in the same type, because these three bodies undergo analogous transformations.

$$\begin{array}{ccccc} \left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O & - & O & = & \left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\} \\ \text{Acetic acid.} & & \text{Oxygen.} & & \text{Aldehyd.} \\ \left.\begin{matrix}H\\H\end{matrix}\right\}O & - & O & = & \left.\begin{matrix}H\\H\end{matrix}\right\} \\ \text{Water.} & & \text{Oxygen.} & & \text{Hydrogen.} \\ \left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O & - & O & = & \left.\begin{matrix}C^2H^5\\H\end{matrix}\right\} \\ \text{Alcohol.} & & \text{Oxygen.} & & \text{Hydride of ethyl.} \end{array}$$

Thus acetic acid may be deprived of its oxygen and give origin to aldehyd ; water may equally lose its oxygen and give rise to free hydrogen ; and alcohol can be deoxidized and furnish hydride of ethyl.

Similarly, when we treat the preceding bodies with perchloride of phosphorus they exchange their oxygen for an equivalent quantity of chlorine, and divide into 2 parts, giving an atom of chlorine to each of their 2 radicles :—

$$\begin{array}{ccccccccc} \left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O & + & PCl^5 & = & PCl^3O & + & \left.\begin{matrix}C^2H^3O\\Cl\end{matrix}\right\} & + & \left.\begin{matrix}H\\Cl\end{matrix}\right\} \\ \text{Acetic acid.} & & \begin{matrix}\text{Perchloride}\\\text{of phosphorus.}\end{matrix} & & \begin{matrix}\text{Oxychloride}\\\text{of phosphorus.}\end{matrix} & & \begin{matrix}\text{Chloride}\\\text{of acetyl.}\end{matrix} & & \begin{matrix}\text{Hydrochloric}\\\text{acid.}\end{matrix} \\ \left.\begin{matrix}H\\H\end{matrix}\right\}O & + & PCl^5 & = & PCl^3O & + & \left.\begin{matrix}H\\Cl\end{matrix}\right\} & + & \left.\begin{matrix}H\\Cl\end{matrix}\right\} \\ \text{Water.} & & \begin{matrix}\text{Perchloride}\\\text{of phosphorus.}\end{matrix} & & \begin{matrix}\text{Oxychloride of}\\\text{phosphorus.}\end{matrix} & & \begin{matrix}\text{Hydrochloric}\\\text{acid.}\end{matrix} & & \begin{matrix}\text{Hydrochloric}\\\text{acid.}\end{matrix} \\ \left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O & + & PCl^5 & = & PCl^3O & + & \left.\begin{matrix}C^2H^5\\Cl\end{matrix}\right\} & + & \left.\begin{matrix}H\\Cl\end{matrix}\right\} \\ \text{Alcohol.} & & \begin{matrix}\text{Perchloride}\\\text{of phosphorus.}\end{matrix} & & \begin{matrix}\text{Oxychloride of}\\\text{phosphorus.}\end{matrix} & & \begin{matrix}\text{Chloride of}\\\text{ethyl.}\end{matrix} & & \begin{matrix}\text{Hydrochloric}\\\text{acid.}\end{matrix} \end{array}$$

By applying the word type in this sense we prejudicate nothing as to the real grouping of the atoms in the molecule, nor the analogy of properties which the bodies may present. We only try to explain the reactions in a more striking manner, and to bring together those which resemble each other.

If two bodies obey two different systems of reaction, they ought to be considered as belonging to two different types.

If a body were to obey at the same time two systems of reaction which characterize different types, it would belong to both these types. Its formula ought to be given differently, according as it would be represented undergoing the one or the other of these two series of reactions.

There is a body, aldehyd, whose formula is generally $\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}$, placing it in the hydrogen type. We thus indicate that this body acts, in a certain number of reactions, like hydrogen; that there is between it and another compound, called acetic acid, the same relation that there is between hydrogen and water.

But if we treat aldehyd by oxychloride of carbon, the following reaction will be produced:—

$$\begin{array}{ccccccccc} C^2H^4O & + & COCl^2 & = & CO^2 & + & \left.\begin{matrix}H\\Cl\end{matrix}\right\} & + & \left.\begin{matrix}C^2H^3\\Cl\end{matrix}\right\} \\ \text{Aldehyd.} & & \text{Oxychloride of carbon.} & & \text{Carbonic anhydride.} & & \text{Hydrochloric acid.} & & \text{Chlor-acetyl.} \end{array}$$

This reaction is analogous to that which takes place when we cause oxychloride of carbon to act on water.

$$\begin{array}{ccccccccc} H^2O & + & COCl^2 & = & CO^2 & + & \left.\begin{matrix}H\\Cl\end{matrix}\right\} & + & \left.\begin{matrix}H\\Cl\end{matrix}\right\} \\ \text{Water.} & & \text{Oxychloride of carbon.} & & \text{Carbonic anhydride.} & & \text{Hydrochloric acid.} & & \text{Hydrochloric acid.} \end{array}$$

When we want to explain this last reaction, the aldehyd ought to receive the formula $\left.\begin{matrix}C^2H^3\\H\end{matrix}\right\}O$, which places it according to the water type.

Gerhardt, after having established the definite meaning of the word type, discovered that all reactions can be referred to four principal types.

These four types are:—

### 1st. The Hydrogen Type $\left.\begin{matrix}H\\H\end{matrix}\right\}$

By substituting simple or compound radicles either for one or both of the atoms of hydrogen, we obtain the formulas—

α. Of simple monatomic bodies.

β. Of compound isolable radicles of the same atomicity.

γ. Of certain bodies formed by the union of two different monatomic radicles, simple or compound.

δ. Of biatomic radicles, simple or compound, of which the molecule is only formed by one atom or by one group in its place.

### 2nd. The Hydrochloric Acid Type $\left.\begin{matrix}\mathrm{Cl}\\\mathrm{H}\end{matrix}\right\}$

All the compounds formed by the combination of chlorine, bromine, iodine, and fluorine, with any monatomic radicle whatever, are considered as belonging to this type. Logically, it is useless; we can include it in the hydrogen type by simply replacing in the latter an atom of hydrogen by an atom of chlorine. Nevertheless, we preserve it because it is useful in practice.

### 3rd. The Water Type $\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}$

In this type are classed the compounds which oxygen, sulphur, selenium, and tellurium form with the different monatomic radicles, and a part of those which these same bodies form with biatomic radicles.

For example, on replacing one H by K (symbol of potassium) we have the compound $\left.\begin{matrix}\mathrm{H}\\\mathrm{K}\end{matrix}\right\}\mathrm{O}$, and on replacing 2H by 2K we have the compound $\left.\begin{matrix}\mathrm{K}\\\mathrm{K}\end{matrix}\right\}\mathrm{O}$.

Lastly, on substituting in these two formulas the symbols of sulphur S, selenium Se, and tellurium Te for that of oxygen, we obtain the formulas

$$\left.\begin{matrix}\mathrm{H}\\\mathrm{K}\end{matrix}\right\}\mathrm{S},\quad \left.\begin{matrix}\mathrm{H}\\\mathrm{K}\end{matrix}\right\}\mathrm{Se},\quad \left.\begin{matrix}\mathrm{H}\\\mathrm{K}\end{matrix}\right\}\mathrm{Te};\quad \left.\begin{matrix}\mathrm{K}\\\mathrm{K}\end{matrix}\right\}\mathrm{S},\quad \left.\begin{matrix}\mathrm{K}\\\mathrm{K}\end{matrix}\right\}\mathrm{Se},\quad \left.\begin{matrix}\mathrm{K}\\\mathrm{K}\end{matrix}\right\}\mathrm{Te},$$

of two sulphur compounds, two selenium compounds, and two tellurium compounds of potassium.

### 4th. The Ammonia Type $\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{N}$

To this type belong the bodies which are derived from ammonia, or the compounds in which the nitrogen of ammonia is replaced by phosphorus, arsenic, antimony, or bismuth.

By the help of the four preceding types we could only represent the formulas and reactions of a very small number of bodies which contain polyatomic radicles. To remedy this inconvenience, Gerhardt invented condensed types, which are only the four preceding ones doubled, tripled, etc.

For these 4 types we have then:

1st. The hydrogen type, simple or condensed—

$$\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\qquad \left.\begin{matrix}\mathrm{H}^2\\\mathrm{H}^2\end{matrix}\right\}\qquad \left.\begin{matrix}\mathrm{H}^3\\\mathrm{H}^3\end{matrix}\right\}\qquad \cdots\cdots \left.\begin{matrix}\mathrm{H}^n\\\mathrm{H}^n\end{matrix}\right\}$$

2nd. The hydrochloric acid type, simple or condensed—

$$\left.\begin{matrix}\mathrm{H}\\\mathrm{Cl}\end{matrix}\right\}\qquad \left.\begin{matrix}\mathrm{H}^2\\\mathrm{Cl}^2\end{matrix}\right\}\qquad \left.\begin{matrix}\mathrm{H}^3\\\mathrm{Cl}^3\end{matrix}\right\}\qquad \cdots\cdots \left.\begin{matrix}\mathrm{H}^n\\\mathrm{Cl}^n\end{matrix}\right\}$$

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3rd. The water type, simple or condensed—

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O,\quad \left.\begin{matrix}H^2\\H^2\end{matrix}\right\}O^2\quad \left.\begin{matrix}H^3\\H^3\end{matrix}\right\}O^3\;\ldots\ldots\;\left.\begin{matrix}H^n\\H^n\end{matrix}\right\}O^n$$

4th. The ammonia type, simple or condensed—

$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\quad \left.\begin{matrix}H^2\\H^2\\H^2\end{matrix}\right\}N^2\quad \left.\begin{matrix}H^3\\H^3\\H^3\end{matrix}\right\}N^3\;\ldots\ldots\;\left.\begin{matrix}H^n\\H^n\\H^n\end{matrix}\right\}N^n$$

Lastly, we are able to join to these types mixed condensed types formed by the union of one or more molecules of water with one or more molecules of hydrochloric acid, as

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O + \left.\begin{matrix}H\\Cl\end{matrix}\right\} = \left.\begin{matrix}H^2\\H\\Cl\end{matrix}\right\}O$$

The discoveries of late years have greatly augmented the importance of these condensed types; it is true that objections have been raised to them on the ground that bodies like water, hydrogen, or ammonia, condensed, do not exist, and therefore cannot serve as types.

This objection is unfounded. The molecular condensations in question could only take place under the influence of polyatomic radicles. Oxygen being saturated in water, we cannot understand why the water should be doubled; but, on the other hand, we can easily conceive that if two atoms of hydrogen taken in two different molecules of water are replaced by an indivisible biatomic radicle, the two molecules of water will be found united into one, as the following formulas will explain:—

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O$$
$$\left.\begin{matrix}H\\H\end{matrix}\right\}O$$

Two molecules of water.

$$\left.\begin{matrix}H\\R''\\H\end{matrix}\right\}O^2$$

Double molecule proceeding from two molecules of water condensed by the biatomic radicle R''.

Sometimes for the hydrogen of one of these types a compound radicle is substituted which itself contains this metalloid. To distinguish the hydrogen which forms part of this radicle from what remains of the primitive formula, this latter receives the name of typical hydrogen.

For instance, on replacing in the formula of water $\left.\begin{matrix}H\\H\end{matrix}\right\}O$, an atom of hydrogen by the radicle ethyl $C^2H^5$, we obtained the formula of alcohol

$$\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O$$

Alcohol.

which contained an atom of typical hydrogen.

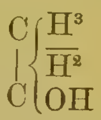
Such was the theory of types in the largest acceptation of the word. We do not hesitate to say that it served its time. What can it explain?

Either a type merely expresses a general system of reactions and serves only to show more clearly the relations which exist between several bodies—in this case it is a mechanical means which renders service, but which has no pretence to be raised to the rank of a theory; or, secondly, a type pretends to unite in one category a series of two bodies fabricated on the same model, and in this case it would, as M. Kolbe remarks, be absurd to suppose that nature is limited to four general plans within which all bodies can be classed; or, finally, types represent the three first degrees of condensation of matter.

This is the opinion which has been finally adopted by M. Wurtz. But it is not difficult to perceive that in this case Gerhardt's types are insufficient. As many would be required as there are different atomicities; and as the condensation of polyatomic radicles may give rise to new radicles of a very high atomicity, the number of types may become indefinite.

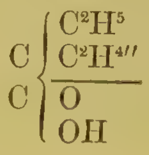
Moreover, already the problem proposed to be solved has changed. The question no longer is to classify reactions, but to determine the intimate structure of the molecule by establishing in what manner the atoms are bound together. Chemistry has already been able to approach this problem, and in many cases, more particularly in organic chemistry, has been able to solve it. Our rational formulas, therefore, no longer represent types of double decomposition; they aim at indicating the bonds which exist between the different atoms constituting a molecule.

To understand these formulas, however complicated they may be, it suffices to know that the polyatomic radicles which are on one side of the bracket serve to join the radicles of different atomicity which are on the other side. Thus the formula $\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O$ signifies that in alcohol 5 atoms of hydrogen are directly united with the carbon, while the sixth atom is only joined to it by the medium of the oxygen. The same fact may be expressed by the more complicated formula



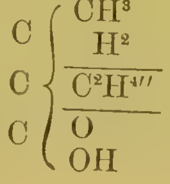
$$\begin{matrix}C\\|\\C\end{matrix}\left\{\begin{array}{l}H^3\\\hline H^2\\OH\end{array}\right.$$

The choice of the rational formula depends on what we want to indicate. In many cases the old typical formulas are sufficient. Sometimes formulas of the kind just given better show the constitution and the system of reactions of a body; but in this case it is usually preferable to employ M. Kékulé's signs, by means of which confusion is more surely avoided. Let us suppose that we wish to give the rational formula of ethyl-crotonic acid $C^6H^{10}O^2$; it may be written in various ways, among which two will seem different, but in reality they indicate the same body. These are the formulas:



$$\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}C^2H^5\\C^2H^{4\prime\prime}\\\hline O\\OH\end{array}\right.$$

and



$$\begin{matrix}C\\C\\C\end{matrix}\left\{\begin{array}{l}CH^3\\H^2\\\hline C^2H^{4\prime\prime}\\\hline O\\OH\end{array}\right.$$

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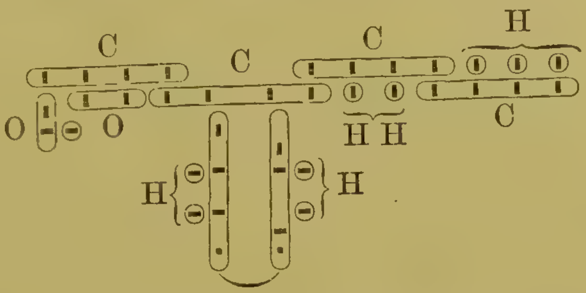
which, given symbolically, take the following form:



We will use all these methods of materializing (so to speak) our thoughts, adopting in each case that which appears the most simple and at the same time the most capable of being understood.

With the theory of types, it would seem logical to abandon the words typical hydrogen, typical oxygen, typical nitrogen, etc. Nevertheless, we will retain it, because it is useful to designate important facts.

We have said that in rational formulas polyatomic radicles placed by the side of a bracket serve to join those placed on the other side, and we have given, as example, the formula of alcohol $\left.\begin{array}{r}C^2H^5\\ H\alpha\end{array}\right\}O$, which indicates that the hydrogen $H\alpha$ differs from that which forms part of the group $C^2H^5$ in that it is only joined to the carbon by means of the oxygen. In whatever way the formula of alcohol may be written, this fact remains the same; and it is, therefore, useful to possess a word to distinguish this atom of hydrogen $H\alpha$ from all the others. The word typical hydrogen having been employed up to the present time in this acceptation, we will retain it.

It is the same with oxygen and nitrogen: we call these bodies typical in every case where, instead of being united by all their centres of attraction to the same polyatomic radicle, they are united by each of these centres to different radicles which they serve to join.

## SALTS, ACIDS, BASES.

When sodium or potassium is made to act on the hydrogen compounds of chlorine, bromine, iodine, or fluorine, or on the more complicated hydrogen compounds which contain oxygen or one of its congeners (sulphur, selenium, tellurium), it always happens in the case of chlorine, bromine, iodine, or fluorine, and often in that of oxygen or analogous compounds, that the metal partially or wholly displaces the hydrogen. This gas then becomes disengaged in a free state, and the metal takes its place.

This reaction is easily produced with water. Submitted to the action of sodium, this liquid exchanges a moiety or the whole of its hydrogen for the metal, giving sodic hydrate or anhydrous oxide of sodium.

$$\underset{\text{Water.}}{2\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Sodium.}}{\left.\begin{matrix}\mathrm{Na}\\\mathrm{Na}\end{matrix}\right\}} = \underset{\text{Sodic-hydrate.}}{2\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{Na}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}}$$

$$\underset{\text{Water.}}{\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}} + \underset{\text{Sodium.}}{\left.\begin{matrix}\mathrm{Na}\\\mathrm{Na}\end{matrix}\right\}} = \underset{\text{Anhydrous oxide of sodium.}}{\left.\begin{matrix}\mathrm{Na}\\\mathrm{Na}\end{matrix}\right\}\mathrm{O}} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}}$$

We may here observe that all the bodies which result from the substitution of a metal for the half of the hydrogen of a molecule of water, or of several molecules of water united, bear the name of hydrates.

The reaction of alkaline metals (potassium, sodium, etc.) on hydrogen compounds is too general to serve as basis for any classification whatever; but the replacing of hydrogen by one of these metals takes place in certain cases by another less general process, which in consequence may become a means of classification.

We may replace the hydrogen of hydrochloric acid by sodium, making the metal act directly on this acid—

$$\underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\text{Sodium.}}{\left.\begin{matrix}\mathrm{Na}\\\mathrm{Na}\end{matrix}\right\}} = \underset{\text{Chloride of sodium.}}{2\left(\left.\begin{matrix}\mathrm{Na}\\\mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}}$$

but we can also arrive at the same result by making hydrochloric acid act on the hydrate of sodium. A double decomposition then takes place, in which chloride of sodium and water are formed—

$$\underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}\mathrm{H}\\\mathrm{Cl}\end{matrix}\right\}} + \underset{\text{Hydrate of sodium.}}{\left.\begin{matrix}\mathrm{Na}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}} = \underset{\text{Chloride of sodium.}}{\left.\begin{matrix}\mathrm{Na}\\\mathrm{Cl}\end{matrix}\right\}} + \underset{\text{Water.}}{\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}}$$

All bodies which, on contact with metallic hydrates, have the property of undergoing a double decomposition, in which the hydrogen which they contain, or at least a part of it, is replaced by a metal at the same time that water is formed, have received the general name of *acids.*

*Acids are, therefore, hydrogen compounds, of which the hydrogen may be wholly or partly replaced by metals, by means of double decomposition with the help of metallic hydrates. Their replaceable hydrogen takes the name of basic hydrogen.*

The hydrates which possess the property of producing double decomposition with the acids have received the generic name of bases.

*Bases, therefore, are hydrates of metals, or compound radicles, capable of exchanging their metal or their radicle for the hydrogen of acids by means of double decomposition.*

We have seen that when we subtract from a compound body one or more of the atoms which constitute it, the residue may be considered as a radicle of precisely equal atomicity to the sum of those of the atoms eliminated.

If, therefore, an acid contains one or more atoms of basic hydrogen, and it be made to lose this hydrogen, the residue will act as a radicle of atomicity equal to the number of atoms of hydrogen lost by the acid.

As an example, let us take sulphuric acid $SO^4H^2$. If $H^2$ be taken from it, the residue $SO^4$ will act as a biatomic radicle. Again, in nitric acid $NO^3H$, on taking away H, we have the residue $NO^3$, which will act as a monatomic radicle. So also in water $H^2O$, if we suppress one atom of hydrogen, we have the monatomic residue OH. M. Cannizzaro proposed giving to these different residues the name of halogen residues. $SO^4$ would then be the halogen residue of sulphuric acid, $NO^3$ that of nitric acid, OH that of water. The same chemist recently proposed to give to this latter residue the special name of hydroxyl, for convenience in speaking. In this case the hydrogen compounds of chlorine and its congeners, and the halogen residues are simple halogen bodies.

This being premised, let us again consider the double decomposition which takes place between an acid and a base, say, between hydrate of potassium and nitric acid—

$$\underset{\text{Nitric acid.}}{NO^3H} + \underset{\text{Hydrate of potassium.}}{KOH} = \underset{\text{Nitrate of potassium.}}{NO^3K} + \underset{\text{Water.}}{HOH}$$

We there see that nitric acid loses its hydrogen H, and the base its metal K; there are, therefore, four residues: on one side the halogen residue $NO^3$ of the nitric acid, and the potassium; on the other hydroxyl OH, and hydrogen. The two first of these residues unite to form nitrate of potassium, and the two latter combine to form water.

It can, therefore, be said, either that the nitrate of potassium results from the substitution of potassium for the basic hydrogen of the nitric acid, or that this body results from the substitution of the halogen residue of the nitric acid for the oxhydryle which the hydrate of potassium contained.

The compounds which result from the reaction of acids on bases have received the name of salts.

Salts may be thus defined: *products which result from the substitution of metals for the basic hydrogen of acids; or products which result from the substitution of the halogen residue of acids for the oxhydryle of bases.*

Besides the reciprocal action which they exercise on each other, and which serves to characterise them, soluble acids and bases have properties which enable them to be readily recognised.

Soluble acids have a sour taste, and possess the property of changing the blue colour of litmus to red. Soluble bases, on the contrary, have an astringent taste, and bring back to blue the litmus reddened by an acid. The action of acids and bases on litmus is explained as follows:

Litmus contains a blue organic salt, the lithmate of lime. When we substitute for the calcium in this body any metal whatever, the blue colour of the compound remains. But if the element substituted be hydrogen, the coloured body, which then takes the name of lithmic acid, becomes red.

The halogen residue which, in the lithmate of lime, is combined with the calcium, and which in lithmic acid is united to the hydrogen, possesses affinities so feeble that it can easily be displaced by the halogen residue of all the other acids, even the weakest. Then the litmus returns to red under the influence of the acids.

On the contrary, if we cause a base to act on the reddened litmus, that is to say on the lithmic acid, a metallic lithmate is formed which is blue, and the litmus regains its original colour.

## CONSTITUTION OF SALTS.

Philosophically, acids and bases ought to be considered as salts. Let us take the last, for example: it is clear that nitrate of potassium is analogous in its constitution to nitric acid and hydrate of potassium; it only differs from the latter in that it contains the halogen residue of an acid instead of that of water, and it differs from the first in that it contains potassium instead of hydrogen, as the electro-positive element. Acids, therefore, are salts which contain hydrogen instead of a metal, as their electro-positive element; and bases are salts which contain hydroxyl instead of the halogen residue of an acid.

Salts are divided primarily into two classes, of which the first contains binary salts; these are the metallic chlorides, bromides, iodides, and fluorides: they have been called by Berzelius, haloid salts. The second class contains the oxy-salts. Each of these latter contains at least three elements. Although the *binary theory of salts*, from which this classification originated, is no longer believed in, yet the classification itself is found exceedingly convenient, and therefore is retained.

## CONSTITUTION OF HALOID SALTS.

The constitution of haloid salts is so simple that it need not detain us long. These result in fact from the juxtaposition of two monatomic radicles. Hydrochloric acid and chloride of potassium may be represented as follows:—

$$\overset{\ominus}{\mathrm{H}}\,\overset{\ominus}{\mathrm{Cl}} \qquad\qquad \overset{\ominus}{\mathrm{K}}\,\overset{\ominus}{\mathrm{Cl}}$$

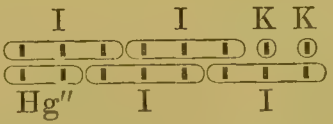
but the constitution of these salts becomes more difficult to explain when they combine to form double salts, as the double chloride of silver and sodium $\left.\begin{matrix}\mathrm{Ag}\\ \mathrm{Cl}\end{matrix}\right\}\left.\begin{matrix}\mathrm{Na}\\ \mathrm{Cl}\end{matrix}\right\}$

Then, the four bodies being monatomic, we do not see what unites the saturated molecule of chloride of silver to the equally saturated molecule of sodic chloride.

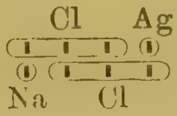
M. Kékulé, to explain this fact, supposes that there exists in chemistry combinations of two orders. According to him, the true chemical combinations formed by the union of atoms must not be confounded with the combinations which result from the union of several molecules, and to which M. Kékulé gives the name of molecular combinations. This theory admitted, we explain by it the double haloid salts, by supposing that they result from the junction of two distinct molecules.

The fact of such molecular combinations cannot be doubted. The existence of water of crystallization (*see* Water of Crystallization) proves it abundantly; but when we consider that these combinations almost always assume either a solid or a liquid state, it is difficult to see how the chlorides can possess such a constitution. M. Deville has, in fact, obtained double chlorides which distil regularly at a very high temperature.

According to my ideas, this is how we may explain the existence of these bodies. Though ordinarily monovalent, iodine has an atomicity really equal to 3. This is deduced from the existence of chloride of iodine $ICl^3$ and of a compound $I\left\{\begin{matrix}OC^2H^3O\\OC^2H^3O\\OC^2H^3O\end{matrix}\right.$ obtained by M. Schützenberger, and which results from the substitution of three atoms of oxacetyl for three atoms of chlorine of the chloride. Being triatomic, iodine may sometimes act with a quantivalence equal to three, and then the double iodides are easy to explain. The bond between the two molecules is the triatomic iodine. The formula $\left.\begin{matrix}Hg''\\I^2\end{matrix}\right\}2\left(\left.\begin{matrix}K\\I\end{matrix}\right\}\right)$ of the double iodide of mercury and potassium may be written in conformity with this theory $\left.\begin{matrix}Hg''\\K^2\end{matrix}\right\}I^4$, and it may be explained by the following symbolical figure:—



This admitted, chlorine, bromine, and fluorine have the greatest analogy with iodine. Though in all cases positively known these bodies are monovalent, it may nevertheless be supposed that they have a real atomicity equal to 3, and that this atomicity, which is nowhere else manifested, shows itself in the double chlorides, bromides, and fluorides. These salts will then answer to formulas analogous to those we have given for the iodide of potassium and mercury. Thus the double chloride of silver and sodium may be represented by the following figure:—



This theory of double haloid salts, though not established by strict proofs, seems to me to be preferable to that given by M. Kékulé.

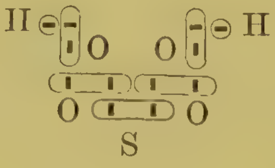
## CONSTITUTION OF OXY-SALTS.

These salts contain never less than three elements, and sometimes more: it will be sufficient if we establish the constitution of ternary salts; those salts which contain four elements and more resembling them precisely.

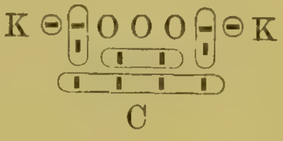
Ternary salts always contain among their elements either oxygen or one of its congeners. A part at least of this oxygen (or its congener) serves to unite the metal to the other simple body or compound radicle which the salt contains, and this union requires as many atoms of oxygen as there are atoms of metal.

Thus sulphuric acid $SO^4H^2$ ought to be written $SO^{2''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.$ to indicate that $H^2$ are united to the group $SO^{2''}$ by the medium of two atoms of oxygen; carbonate of potassium $CO^3K^2$ ought to be $CO''\left\{\begin{matrix}OK\\OK\end{matrix}\right.$ to show that it is by the medium of the oxygen that $CO''$ is joined to $K^2$.

The following figures render this constitution easy to be understood:—



$SO^4.H^2$



$CO^3.K^2$

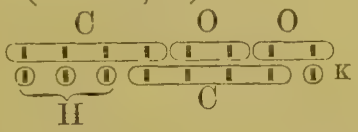
But it is not sufficient to affirm that in salts the metal is united to the metalloid by the medium of oxygen or of one of its congeners, an experimental demonstration must be given of this fact, and the most conclusive is the action which perchloride of phosphorus ($PCl^5$) exercises on the acids and oxygenized bodies in general.

This action consists in the perchloride of phosphorus taking an atom of oxygen to form oxy-chloride of phosphorus ($PCl^3O$), while the two atoms of chlorine, abandoned by the perchloride, are substituted for the atom of oxygen which the oxygenized body has lost.

$$\underset{\text{Aldehyd.}}{(C^2H^4O)} + \underset{\substack{\text{Perchloride}\\ \text{of phosphorus.}}}{(PCl^5)} = \underset{\substack{\text{Oxychloride}\\ \text{of phosphorus.}}}{(PCl^3O)} + \underset{\substack{\text{Chloride of}\\ \text{Ethylene.}}}{(C^2H^4Cl^2)}$$

Every time that oxygen, which is biatomic, has its two centres of affinity saturated by one radicle it is evident that the two atoms of chlorine take its place; that is to say, they combine with this radicle, forming a single compound, as in the example just given.

If, on the contrary, the oxygenized compound contains two radicles united by the medium of the oxygen; that is to say, if each of the two centres of affinity of the oxygen is united to a different radicle, as in the acetate of potassium $\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right)$

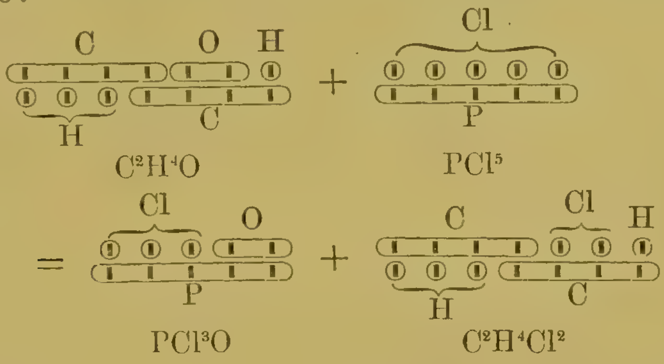


when chlorine is substituted for the oxygen, these two radicles separate, the monatomic chlorine not being able to unite them as did the biatomic oxygen. Then we obtain two different chlorinated bodies, or two molecules of the same chlorinated body, if there is identity between the two radicles combined with the oxygen.

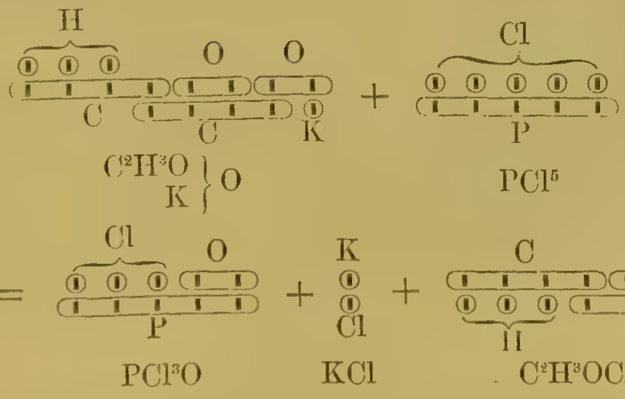
$$\underset{\text{Acetate of potassium.}}{\left(\left.\begin{matrix}(C^2H^3O)\\K\end{matrix}\right\}O\right)} + \underset{\text{Perchloride of phosphorus.}}{(PCl^5)} = \underset{\text{Oxychloride of phosphorus.}}{(PCl^3O)} + \underset{\text{Chloride of potassium.}}{\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)} + \underset{\text{Chloride of acetyl.}}{\left(\left.\begin{matrix}C^2H^3O\\Cl\end{matrix}\right)\right\}}$$

The following symbolical designs show clearly the difference between the two reactions which we have given as examples.

1st. Example :—

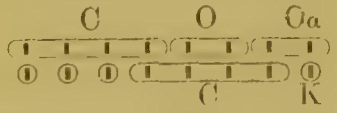


2nd. Example :—

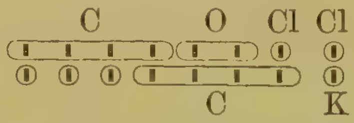


$\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O$

It is clear that if in the compound $\left(\left.\begin{matrix}(C^2H^3O)\\K\end{matrix}\right\}O_a\right)$



two atoms of chlorine were substituted for the atom of oxygen *a* which unites the potassium K to the group ($C^2H^3O$), the molecule would be found represented by the following figure :



This figure shows that the atom of chlorine and the atom of potassium which are on the right, not being joined to the remainder of the molecule, ought to be separated from it. This is what really takes place.

The reaction which the perchloride exercises on oxy-salts shows that these bodies always contain at least two simple or compound radicles united by means of oxygen. Of these radicles, the one which has no metallic properties takes the name of the acid radicle. These radicles generally receive names which are formed by substituting the termination *yl* in place of the terminations of the generic names of the salts of which they form a part. Thus the acid radicle ($C^2H^3O$) which acts in the acetates has received the name of *acetyl.*

The halogen residues of acids are only the radicles of these acids, plus the oxygen destined to unite these radicles to the metals. In each case they receive a particular name, which is made by prefixing *oxy* to the name of the radicle which the halogen residue contains.

Thus the radicle ($C^2H^3O$) of acetates joined to O forms the halogen residue of acetic acid ($C^2H^3OO$), the radicle ($C^2H^3O$) having received the name of acetyl, the halogen residue ($C^2H^3OO$) is called oxyacetyl, or more simply oxacetyl.

## NEUTRAL, ACID, BASIC, AND DOUBLE SALTS.

When the radicle of an acid is monatomic, a single atom of hydrogen may be united to it by the medium of oxygen. The acid which is derived from this radicle then contains a simple molecule of hydroxyl, and is called monatomic. When, on the contrary, the radicle of an acid is polyatomic, each of its free centres of attraction is saturated by hydroxyl OH, the acid then contains a number of molecules of hydroxyl equal to that which indicates the atomicity of the radicle, it is called polyatomic, and the degree of its atomicity is determined by the number of molecules of hydroxyl which it contains.

Acetic acid ($C^2H^3O$), ($OH$) is monatomic, sulphuric acid $\left(SO^{2''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)$ biatomic, phosphoric acid $\left(PO'''\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.\right)$ triatomic, etc.

It is the same with bases. If a metal is monatomic, it can only fix a single halogen residue of water; if it is biatomic, it will fix two; if triatomic, three, and so on. In the first case, bases are called monatomic, and in the others polyatomic. Here again the degree of their atomicity is determined by the number of molecules of hydroxyl which they contain. Thus the hydrate of potassium (KOH) is monatomic, the hydrate of barium $\left(Ba'' \left\{ \begin{matrix} OH \\ OH \end{matrix} \right.\right)$ biatomic, ferric hydrate $\left(Fe^2 \left\{ \begin{matrix} OH \\ OH \\ OH \\ \hline OH \\ OH \\ OH \end{matrix} \right.\right)$ hexatomic, etc.

These denominations are evidently bad. We have seen that the words mono, bi, tri, atomic have quite another meaning. It would be much better, as M. Rogoïsky advised, to call acids and bases mono, bi, tri, hydrique, to express how many halogen residues of water OH these bodies contain. Nevertheless, the words mono, bi, tri, atomic being so univerally used, we must conform to the usage, but must point out that it is very important not to confound the two meanings attributed to the word *atomicity*. This confusion is easy to avoid because one of the acceptations of the word is only applied to radicles, while the other applies to the molecules which contain hydroxyl.

In an acid, the hydrogen of the hydroxyl, otherwise called typical hydrogen, can be wholly or partially replaced by a positive radicle. When the hydrogen is wholly replaced, the salts are called *neutral*, because they no longer possess any of the properties which characterize acids.

When the typical hydrogen is only partially replaced, the salts which are formed still retain acid properties, and are therefore called *acid salts.*

Thus, in sulphuric acid $\left(SO^{2''} \left\{ \begin{matrix} OH \\ OH \end{matrix} \right.\right)$, an atom of a metal can be substituted for an atom of hydrogen, or two atoms of a metal for two atoms of hydrogen.

The salt which is obtained in the first case $\left(SO^{2''} \left\{ \begin{matrix} OK \\ OH \end{matrix} \right.\right)$ is an acid salt, and in the second case $\left(SO^{2''} \left\{ \begin{matrix} OK \\ OK \end{matrix} \right.\right)$ a neutral salt.

Whatever may be the number of atoms of typical hydrogen which an acid contains, this acid can never give, with one metal, more than one neutral salt, while the number of acid salts that it can form is equal to the number which expresses its atomicity, less one.

Bases also, in double decompositions, may undergo the replacement of the whole or of a part of their typical hydrogen by the radicle of an acid. The salts which result are neutral when the whole of their typical hydrogen is thus replaced; but when the substitution affects only a part of this element the salts formed retain their basic properties, and are therefore termed basic salts.

Thus in hydrate of barium $\left(Ba'' \left\{ \begin{matrix} OH \\ OH \end{matrix} \right.\right)$ the two atoms of hydrogen may be replaced by the radicle of acetic acid, acetyl $(C^2H^3O)$; the compound $\left(Ba'' \left\{ \begin{matrix} (OC^2H^3O) \\ (OC^2H^3O) \end{matrix} \right.\right)$ which results from this reaction is a neutral salt. But acetyl may only be substituted for a single atom of hydrogen, and then we have the basic salt $\left(Ba'' \left\{\begin{matrix} OC^2H^3O \\ OH \end{matrix}\right.\right)$.

When the different atoms of typical hydrogen of acids or bases are replaced by different radicles, the salts which result from these substitutions are called double salts.

Sulphate of potassium and sodium $\left(SO^{2''} \left\{\begin{matrix} OK \\ ONa \end{matrix}\right.\right)$ is a double salt. It would be the same of a body which should have for formula

$$\left(Pb'' \left\{\begin{matrix} ONO^2 \\ OC^2H^3O \end{matrix}\right.\right)$$

Aceto-nitrate of lead (hypothetical).

Certain acid or basic salts, submitted to the action of heat, lose water and give rise to new salts, which used to be called *anhydrous acid salts* or *anhydro-salts.* Thus the acid sulphate of sodium $\left(SO^{2''} \left\{\begin{matrix} ONa \\ OH \end{matrix}\right.\right)$, when heated, loses water, and gives the salt

$$\left(\begin{matrix} SO^{2''}\left\{\begin{matrix} ONa \\ \end{matrix}\right. \\ \qquad O \\ SO^{2''}\left\{\begin{matrix} ONa \end{matrix}\right. \end{matrix}\right)$$

These compounds, as we clearly see from the discoveries in organic chemistry made by M. Wurtz and M. Lourenço, are really neutral salts derived from particular acids or bases differing from those which gave origin to the primitive salts. The compound $\left(\begin{matrix} SO^{2''}\left\{ONa\right. \\ \qquad O \\ SO^{2''}\left\{ONa\right. \end{matrix}\right)$, for example, is derived from the acid $\left(\begin{matrix} SO^{2''}\left\{OH\right. \\ \qquad O \\ SO^{2''}\left\{OH\right. \end{matrix}\right)$.

Certain acids have this remarkable property, that all their atoms of typical hydrogen cannot be replaced by positive metals. Then we say that their basicity is less than their atomicity, and the number which expresses their basicity is that of their atoms of hydrogen capable of being replaced.

Lactic acid $\left(C^3H^4O'' \left\{\begin{matrix} OH \\ OH \end{matrix}\right.\right)$ contains two atoms of typical hydrogen; it is therefore biatomic. But only one of these atoms of hydrogen can be replaced by a positive metal. This acid is therefore monobasic.

When, on the contrary, the whole of the typical hydrogen of an acid can be exchanged for positive metals by double decomposition, we say that its basicity equals its atomicity.

Analogy shows us polyatomic bases whose typical hydrogen can only be partially replaced by acid radicles. Then we say that their acidity is less than their atomicity. A base $\left(R''' \left\{\begin{matrix} OH \\ OH \\ OH \end{matrix}\right.\right)$, in which $H^2$ can only be replaced by negative radicles, will be triatomic and biacid.

When salts react upon each other, they give rise to double decompositions which we can generally foresee by bearing in mind the two laws which we are going to explain, and the discovery of which is due to Berthollet.

**Berthollet's Laws.**—When we cause two salts to react (by salts we mean both acids and bases) by means of a solvent, if, by double decomposition, a new salt can be produced less soluble than those which we have mixed, this salt will be produced.

When we apply dry heat to two salts, if, by double decomposition, a new salt can be produced more volatile than the salts previously mixed, this salt will be produced.

*Example:* If we mix a solution of chloride of barium $\left(Ba''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)$ with a solution of sulphate of zinc $\left(\left.\begin{matrix}SO^{4''}\\Zn''\end{matrix}\right\}\right)$, as a double decomposition between these bodies would produce sulphate of barium and chloride of zinc, according to the equation:

$$\underset{\text{Chloride of barium.}}{\left(Ba''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)} + \underset{\text{Sulphate of zinc.}}{\left(\left.\begin{matrix}SO^{4''}\\Zn''\end{matrix}\right\}\right)} = \underset{\text{Chloride of zinc.}}{\left(Zn''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)} + \underset{\text{Sulphate of barium.}}{\left(\left.\begin{matrix}SO^{4''}\\Ba''\end{matrix}\right\}\right)}$$

and as, further, the sulphate of barium is insoluble, the double decomposition takes place.

So, if we heat sulphate of ammonium with chloride of barium, there will be produced sulphate of barium and chloride of ammonium, on account of the volatility of this latter salt, according to the equation:

$$\underset{\text{Sulphate of ammonium.}}{\left(SO^{2''}\left\{\begin{matrix}ONH^4\\ONH^4\end{matrix}\right\}\right)} + \underset{\text{Chloride of barium.}}{\left(Ba''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)} = \underset{\text{Sulphate of barium.}}{\left(SO^{2''}\left\{\begin{matrix}O\\O\end{matrix}\right\}Ba''\right)} + 2\underset{\text{Chloride of ammonium.}}{\left(\left.\begin{matrix}NH^4\\Cl\end{matrix}\right\}\right)}$$

The following is the explanation of these two laws:

Every time that two salts are brought together, and whatever may be their solubility or their volatility, a double decomposition takes place, and there is a division between the negative radicles and the positive radicles. Thus, if we cause sulphate of sodium $\left(SO^{2''}\left\{\begin{matrix}ONa\\ONa\end{matrix}\right.\right)$ to react with chloride of potassium $\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)$, there is produced a mixture of these two salts, giving sulphate of potassium $\left(SO^{2''}\left\{\begin{matrix}OK\\OK\end{matrix}\right.\right)$, and chloride of sodium $\left(\left.\begin{matrix}Na\\Cl\end{matrix}\right\}\right)$.

$$2\underset{\text{Sulphate of sodium.}}{\left(SO^{2''}\left\{\begin{matrix}ONa\\ONa\end{matrix}\right.\right)} + 4\underset{\text{Chloride of potassium.}}{\left(\begin{matrix}K\\Cl\end{matrix}\right)}$$

$$= \underset{\text{Sulphate of potassium.}}{\left(SO^{2''}\left\{\begin{matrix}OK\\OK\end{matrix}\right.\right)} + \underset{\text{Sulphate of sodium.}}{\left(SO^{2''}\left\{\begin{matrix}ONa\\ONa\end{matrix}\right.\right)} + 2\underset{\text{Chloride of potassium.}}{\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)} + 2\underset{\text{Chloride of sodium.}}{\left(\left.\begin{matrix}Na\\Cl\end{matrix}\right\}\right)}.$$

Then if all these new salts are soluble they will remain in solution; and unless they have different colours from the primitive ones, there will be nothing perceptible to indicate the change which has taken place. It will be the same if we operate by means of dry heat, and all the products are fixed. But if one of the salts be, in the first case, insoluble, or in the second volatile, it will be precipitated or evaporate, and the equilibrium will be destroyed, as one of the terms which should serve to constitute it will be wanting. A second division will occur between the elements which remain; the new quantity of insoluble or volatile salt will in its turn be eliminated. A third division succeeds to the second, and the process will continue until the whole of the radicles, which by their union formed an insoluble or volatile salt, are eliminated.

According to M. Malaguti, when a division between two different salts thus occurs, the quantities of salts which are formed are not equivalent to each of the primitive ones, but seem to be proportional to the force with which their elements are capable of entering into combination.

For example, if we have two salts, one of which is formed by the union of the electro-positive radicle A with the electro-negative radicle B, and the other by the combination of the electro-negative radicle B with another electro-positive radicle A′, the force with which the radicle A is capable of uniting with the radicle B being to that of the radicle A′ as 3 : 2, the quantities of $A+B$ and $A'+B$ which arise will also be as 3 : 2.

Let us suppose that we mix 100 molecules of acetate of barium $\left(Ba''\left\{\begin{matrix}OC^2H^3O\\OC^2H^3O\end{matrix}\right.\right)$ and 100 molecules of neutral nitrate of lead $\left(Pb''\left\{\begin{matrix}ONO^2\\ONO^2\end{matrix}\right.\right)$. We shall see by experiment that a double decomposition takes place between 77 molecules of each of these salts. This number 77, which expresses the molecular quantity of the two salts which mutually decompose, is called the coefficient of decomposition of the two saline bodies.

If we reverse the preceding experiment; that is to say, if we mix 100 molecules of nitrate of barium $\left(Ba''\left\{\begin{matrix}ONO^2\\ONO^2\end{matrix}\right.\right)$ and 100 molecules of acetate of lead $\left(Pb''\left\{\begin{matrix}OC^2H^3O\\OC^2H^3O\end{matrix}\right.\right)$, only 22 molecules of each kind will undergo decomposition. This figure 22 will be the coefficient of decomposition of the two new saline bodies. As, added to the preceding, it gives 100, we conclude that, whatever may be the two bodies reacting on each other, the proportions of the salts which arise from the reciprocal exchange of the radicles will be invariably the same. We express this fact as follows:

*The coefficients representing the quantities of salts decomposed in two saline couples containing the same radicles grouped in inverse order, are complementary.*

**Action of Electricity on Salts.**—When a current of electricity is powerful enough to decompose a salt, the electro-positive element goes to the negative pole and the negative group goes to the positive pole.

If we submit sulphate of copper ($SO^{4''}Cu''$) to the action of a current, the metallic copper will be deposited at the negative pole, while the group $SO^{4''}$ goes to the positive pole decomposing the water by taking its hydrogen to reform the sulphuric acid ($SO^{4''}H^2$) while the oxygen is set free.

In the case of the salts of potassium or sodium, the fact is more difficult to state; the metal set free decomposing the water giving hydrate of potassium (KHO) and free hydrogen. Thus, when we decompose the sulphate of potassium $\left(SO^{2''}\left\{\begin{matrix}OK\\OK\end{matrix}\right.\right)$, we find at the positive pole oxygen and sulphuric acid, as in the preceding case; but at the negative pole, we collect, instead of the metal, hydrate of potassium and hydrogen.

Chemists formerly attributed the oxygen and hydrogen disengaged in this reaction to the decomposition of water. As to the salt, they supposed it to be decomposed into sulphuric anhydride ($SO^3$) and oxide of potassium ($K^2O$), bodies which, when joined to water, form hydrated sulphuric acid and hydrate of potassium.

The following experiment has condemned this interpretation, and shows that the facts occur as we have already indicated.

Place a concentrated solution of sulphate of potassium $\left(SO^{2''}\left\{\begin{matrix}OK\\OK\end{matrix}\right.\right)$ over mercury, and cause a strong current to pass through this liquid, taking care that the negative wire is plunged into the mercury. The potassium set free then combines with this latter metal, and the amalgam formed not being acted on by water, as is the pure potassium, after some time we can collect a certain quantity of this body by evaporating the mercury.

The phenomenon is, therefore, the same as that produced with the sulphate of copper, and the apparent difference of the result is only owing to the secondary action which the alkaline metal exercises on water.

## NOMENCLATURE.

Chemical nomenclature originated at the close of the last century. The first system was proposed by Guyton de Morveau, and the definitive nomenclature was resolved upon by a commission of which Lavoisier formed one.

Nomenclature having arisen at an epoch when organic chemistry was almost entirely unknown, it only applies to mineral compounds, or rather, if it be applied to the combinations which organic radicles form, the names of these radicles are fixed in an entirely arbitrary manner.

Nomenclature does not express in mineral chemistry all that we ought to expect of it. A great number of facts discovered since its origin render it incomplete.

We will here explain what it is, making our explanation as much as possible in harmony with the theories professed by the majority of chemists at the present time.

**Names of Simple Bodies.**—The names of simple bodies are absolutely arbitrary. To designate these bodies we generally choose words which refer to some of their properties. Bromine comes from the Greek *βρωμος*, a "stench;" iodine, from *ἰωδης*, "violet," on account of the beautiful violet colour of the vapour of this metalloid.

The names of the various compound bodies are usually derived from those of their more simple components.

**Names of Binary Compounds.**—1st. *General Rule.*—We designate by the termination *ide* the name of the electro-negative body of the compound, and follow it by the name of the electro-positive body. Thus, a compound of chlorine and iron is called *chloride of iron;* a compound of sulphur and copper, *sulphide of copper*, etc.

To this first rule, which enables us to perceive the qualitative composition of a body simply from the inspection of its name, is added another, which aims at making known its quantitative composition also.

If an electro-negative element be monatomic, we place before the generic name of the compound the prefixes *mono*, *bi*, *tri* or *ter*, *tetra*, *sesqui*, etc.; *mono*, if, for an electro-positive atom, the compound contains a single electro-negative atom; *bi*, if it contains two; *tri*, if it contains three; *tetra*, if it contains four; *sesqui*, if it contains three for two of the electro-positive body.*

Thus the compound KCl is called monochloride, or simply chloride of potassium; the compound $Hg''Cl^2$, bichloride of mercury; the compound $Au'''Cl^3$, terchloride of gold; the compound $CCl^4$, tetrachloride of carbon, etc.

If the electro-negative body be biatomic, we place before the generic name of the compound the syllables *mono*, *bi*, *tri*, *tetra*, *sesqui*, etc.

The prefix *mono* is employed when the compound contains a single atom of the electro-negative body, either for one of the electro-positive body, if this has an even atomicity, or for two if it has an uneven atomicity; the prefix *bi*, when the compound contains two atoms of the electro-negative body for one of the electro-positive body, if this has an even atomicity, or for two if it has an uneven atomicity, etc.

The prefix *sesqui* is applied to bodies in which, for two positive atoms of even atomicity, or for a double number of positive atoms of uneven atomicity, there are three negative atoms.

Lastly, if for a single negative atom there are more than one or two positive atoms, according to the atomicity, the name of the compound ought to be preceded by the prefix *sub*.

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* Since the adoption of the new atomic weights, there no longer exists any formula of this latter kind, it having been discovered that the bodies which were believed to have such formulæ possess a different constitution.

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*Ex.:* $K^2S$ is called monosulphide of potassium.
$Na^2S^2$ — bisulphide of sodium.
$Na^2S^3$ — trisulphide of sodium.

$Ba''S$ is monosulphide of barium.
$Ca''S^2$—bisulphide of calcium.
$Fe^2S^3$—sesquisulphide of iron.
$Hg^2S$—subsulphide of mercury.

Whatever may be the atomicity of the elements which enter into a binary compound, when the generic name is preceded by the prefix *per* or *hyper* it indicates of all the combinations which the two components can form, the one which contains the largest proportion of the negative element. Thus the compound $Fe^2Cl^6$ is called perchloride of iron; the compound $K^2S^5$, persulphide of potassium.

When the electro-negative body has an atomicity greater than two, the quantities of it are no longer indicated.

2nd. *First exception.*—This affects the hydrogenized compounds. Three cases may arise: when these compounds are strongly acid, when they are neutral, or when they have a weak acidity.

*When they are strongly acid* they are called acids, and the prefix *hydro* is placed before the name of the electro-negative body of the combination: thus—

The compound HCl is hydrochloric acid.
The compound HBr is hydrobromic acid.

*When they are neutral* their name is generally according to the rule, but sometimes the prefix *hydro* is placed before the name of the electro-negative body. Sometimes the termination "uretted" replaces the last syllable of the electro-negative body: thus $CH^4$ may be called a carbide of hydrogen, or a hydro-carbon or carburetted hydrogen.

*When they are slightly acid* they sometimes follow the rule for those which are strongly acid; at others, the last syllable of the name of the electro-negative body is replaced by the termination "uretted:" thus $H^2Se$ is hydro-selenic acid, or seleniuretted hydrogen.

3rd. *Second Exception.*—The second exception has reference to the combinations of metals with one another. These combinations are named alloys. Thus we say alloy of iron and copper, alloy of zinc and lead. The alloys into which mercury enters are named amalgams. An alloy of mercury and silver is called silver amalgam.

4th. *Third Exception.*—The third exception, by far the most important, has reference to oxygenated compounds. When an oxygenated compound is capable by a reaction with the elements of water of forming an acid it is called an *anhydride*; and this word is placed after the name of the acid. Thus the compound of phosphorus and oxygen ($P^2O^5$) is named phosphoric anhydride, because, by reacting with water, it produces phosphoric acid.

If the oxygenated compound does not undergo reaction with water, but reacts with bases to form salts, its name is made according to the preceding exception. Thus we cause the word anhydride to follow the name of the hypothetical acid which we obtain by replacing by hydrogen the metals of the salts to which this binary compound gives origin. For example:

Carbon and oxygen form a compound $CO^2$ which, by acting on bases, furnishes salts, of which the formula is $(CO^3M'^2)$, $M'$ being a monatomic metal.

The acid which would be obtained by substituting $H^2$ for $M^2$ would have the following formula $(CO^3H^2)$. If it existed, its name, according to the preceding rules, would be *carbonic acid.* The compound $CO^2$ would then be called carbonic anhydride.

Instead of naming the preceding bodies as above, we often call them *anhydrous acids.* Instead of saying *phosphoric anhydride* and *carbonic anhydride*, we may say *anhydrous phosphoric acid* and *anhydrous carbonic acid.* The former names are to be preferred, because they are more in harmony with modern theories. In fact, binary compounds cannot be acid unless they contain hydrogen.

When binary oxygenated compounds are not able to react upon water to form acids, nor upon bases to form salts, they are called oxides, and the particle *of* is placed after this word (oxide), being itself followed by the name of the simple body combined with oxygen. Thus the compound of oxygen and potassium $K^2O$ is named oxide of potassium.

Since the same simple body is able to form several binary compounds with oxygen, it is convenient, in order to distinguish them from one another, to precede the word oxide by the prefixes *prot*, *bin*, *ter*, *tetra*, *sesqui*, *sub*, *per.*

These prefixes indicate the same relation between the oxygen and the body to which it is united as they do between the biatomic electro-negative bodies and electro-positive bodies, which we have already explained.

Thus the compounds $(K'^2O)$, $(Cu''O)$, $(Hg''O)$, are named protoxides of potassium, of copper, and of mercury.

The compounds $(Mn''O^2)$, $(Ba''O^2)$, are named binoxides of manganese and of barium.

The compound $\left(\begin{matrix}Au''' \\ Au'''\end{matrix}\right\}O^3\Big)$ is teroxide of gold.

The compound $(Fe^{2\text{vi}}O^3)$ is sesquioxide of iron.

The compound $(Hg^2O)$ is suboxide of mercury.

Sometimes the word peroxide is used to designate the oxide containing the most oxygen which a body is able to bear without forming an anhydrous acid.

In the second of the preceding examples, we may either say binoxide or peroxide of manganese, binoxide or peroxide of barium. Experience shows that $(Ba''O^2)$ is the compound of barium which contains the largest quantity of oxygen, and that $(Mn'O^2)$ is the compound of manganese which contains the most oxygen without being an anhydrous acid.

5th. *Fourth Exception.*—Among the bodies whose nomenclature obeys the ordinary rules are found the binary compounds of sulphur, selenium, and tellurium. Some of these present the same relation to certain sulphuretted, seleniuretted, or telluretted acids as the oxygenated anhydrides do to the acids which are derived from them. We then name these bodies at will, either according to the general rule, or by causing the word anhydrosulphide to follow the name of the acids to which they correspond. The body ($CS^2$) differing from sulpho-carbonic acid ($CS^3H^2$) by ($H^2S$) in the same manner as carbonic anhydride ($CO^2$) differs from the hypothetical carbonic acid ($CO^3H^2$), viz., by ($H^2O$), may be called bisulphide of carbon, or sulphocarbonic anhydrosulphide.

**Ternary Compounds.**—All the ternary compounds whose nomenclature follows the rules are salts, which are sometimes oxygenated, sometimes not: the rules are different in the two cases.

1st. WHEN THE SALTS ARE OXYGENATED.—To these a generic name is given which is common to all those which contain the same halogen residue, and a specific name to distinguish between the different species of the same class.

*Formation of the Name of the Class.*—This is effected by replacing the last syllable of the name of the simple body which is united to oxygen in the halogen residue by the terminations *ate* or *ite*.

When two classes of salts only differ from one another by the quantity of oxygen which they contain, the termination *ate* is given to the class containing the most oxygen, and that of *ite* to the less oxygenated class.

There are often more than *two* classes of salts which only differ from one another by the quantity of oxygen which they contain. We then form the name of the class of those in which the halogen residue contains more oxygen than the class terminating in *ite*, but less than that terminating in *ate*, by placing the prefix *hypo* before the name terminating in *ate*.

We place the same prefix *hypo* before the name terminating in *ite* to designate a class of salts less oxygenated than that which answers to this termination.

Lastly, to indicate a class of salts more oxygenated than that which has received the termination *ate*, we place before the name of this latter class the prefixes *per* or *hyper*.

Thus there is a class of salts of which the halogen residue is constituted by chlorine and oxygen. In this class there are five sub-classes, viz.:

| | |
|---|---|
| The class hypochlorite . . . . . . . . . . | $ClO—R'$. |
| The class chlorite . . . . . . . . . . . | $ClO^2—R'$. |
| The class hypochlorate (*this class does not exist; we assume it in order to demonstrate the rules of nomenclature*) . . . . . . . . . . . | $Cl^2O^5—R'$. |
| The class chlorate . . . . . . . . . . . | $ClO^3—R'$. |
| The class perchlorate . . . . . . . . . | $ClO^4—R'$. |

Thus we see the class hypochlorite is the least oxygenated, and that the quantity of oxygen augments progressively in the following classes which correspond to the names chlorite, hypochlorite, chlorate, and perchlorate.

*Formation of the Specific Name.*—The specific name is no other than that of the simple body or of the electro-positive radicle: thus, reproducing the preceding examples:

If in the class chlorate we place a definite radicle, as potassium, sodium, or silver, in the place of the R′ we shall have—

| | |
|---|---|
| Chlorate of potassium . . . . . . . . . . | $ClO^3, K.$ |
| Chlorate of sodium . . . . . . . . . . . | $ClO^3, Na.$ |
| Chlorate of silver . . . . . . . . . . . . | $ClO^3, Ag.$ |

It may happen that the same electro-positive radicle makes two different kinds of salts with one and the same negative group; to distinguish between them we then add to the specific name the words *ad maximum* or *ad minimum.* The salts "ad maximum" are those into which the largest proportion of the negative group enters; while the salts "ad minimum" are those into which the smallest proportion of it enters. Generally, however, the prefix "per" is used for the "ad maximum" compound, and those of "proto" or "sub" for the "ad minimum."

For example, there are two sulphates of iron:

The sulphate ad maximum, or persulphate = $(Fe^2(SO^4)^3)$.
The sulphate ad minimum, or protosulphate = $(FeSO^4)$.

2nd. THE SALTS ARE NOT OXYGENATED.—If these salts contain sulphur, selenium, or tellurium in the negative group, their name will be formed in the same manner as if they were oxygenated; only we precede the generic name by the prefixes sulpho, selenio, or tellurio, to indicate which of these bodies replaces the oxygen. Thus the class $CO^3R^2$ being called carbonate, the class $CS^3R^2$ will be called sulphocarbonate.

If the salts do not contain either oxygen, sulphur, selenium, or tellurium, two cases may occur: in the first, there will be two positive elements for one negative; in the second, there will be one positive and two negative elements.

When there is one negative element, we replace the last syllable of its name by *ide*, and place the word *double* before it; after the termination *ide* are placed the names of the two positive bodies: thus the body $\left.\begin{matrix}AgNa\\ Cl^2\end{matrix}\right\}$ is called the "double chloride of silver and sodium."

If, on the contrary, the body contains one positive element and two negative ones, we cause the name of one of these latter to terminate in "*o*," and join to it the name of the other with the termination *ide*, and then place the name of the positive element; thus the body $\left.\begin{matrix}Hg\\ ICl\end{matrix}\right\}$ is named the "iodo-chloride of mercury."

When the salts are sulphuretted, seleniuretted, or telluretted, names are chosen deduced from the preceding rules. For example, the salt

$(CS^3K^2)$ may be be called the double sulphide of potassium and carbon, or sulphocarbonate of potassium. The latter of these names is preferable, and will end in being the only one used.

3rd. ACIDS, BASES.—The salts which contain hydrogen as their electro-positive element are called *acids*. They are named by causing this latter word to follow the generic name of the salts which correspond to them, after having changed the termination "*ate*" into "*ic*," and that of "*ite*" into "*ous*."

The acid which corresponds to chlorates is chloric acid; to chlorites, chlorous acid; and to sulphocarbonates, sulphocarbonic acid, etc.

When the group HO constitutes the electro-negative element of a salt, this salt is a base; the generic name of "*hydrate*" is given to this class of salts, and their specific names are formed as in the other cases. The compound (KHO), formerly hydrate of potash, ought to be called "hydrate of potassium."

**Quaternary Compounds.**—Quaternary compounds are salts which contain sometimes one negative group to two positive radicles, sometimes one positive radicle to two negative radicles, and sometimes one ternary negative radicle and one positive radicle.

1st. *There is one negative radicle to two positive radicles.*—If hydrogen be not found in the positive radicles, the name of the salt is formed in the ordinary manner, with the exception that the word double is placed before the generic name of the body. Thus the body $(SO^{4''},K,Na)$ is named double sulphate of potassium and sodium.

If hydrogen is one of the positive elements we have an acid salt; we then place the word "acid" before the generic name, or we add the prefix *bi* to the generic name.

Thus two sulphates of potassium are known; one neutral $(SO^{4''}K^2)$, the other acid $(SO^{4''}KH)$. The latter is named acid sulphate, or bisulphate of potassium. When the acid salt contains several atoms of hydrogen, the number of them is indicated by the syllables *mono*, *bi*, *tri*, *tetra*, placed before the generic name.

2nd. *There is one positive radicle to two negative radicles.*—If hydroxyl (HO) does not exist in the negative radicles, the last syllable of one of these radicles is changed into *o*, and the name of the second radicle, terminated by the syllable *ate* or *ite*, according to the ordinary rules, is joined to it.

Thus the compound $(NO^2,ClO^2,Pb'')$ is named the chloro-nitrate of lead.

When the group (HO) is one of the negative radicles, the salt is named as if it only contained the other negative radicle, and the word basic is placed before the generic name of the salt; or, as is more general, the prefix *sub* is used.

Thus, there are two nitrates of bismuth; the one $(NO^3,{}^3Bi''')$ neutral, the other $(NO^3(HO)^2Bi''')$ basic: the latter is named the basic nitrate, or subnitrate of bismuth.

If the salt contain several molecules of the group (HO), the prefixes *mono*, *bi*, *tri*, *tetra*, according to the case, are added to the word basic.

3rd. *There is one positive radicle and one ternary negative radicle.*—In this case the generic name is made as usual, but it has certain prefixes attached to it. These prefixes indicate the nature of the bodies taking the part of the negative group, the last of which in the name has the termination *ate:* thus the salt $(CO^2S,K^2)$ is called binoxysulphocarbonate of potassium.

**Bodies which contain more than Four Elements.**—These compounds have the same rules of nomenclature as the quaternary ones. For example, the salt $(PO^{4''},Na,K,Li)$ has the name of phosphate of potassium, sodium, and lithium; the compound $(PO^{4'''},SO^{4''},NO^3,Fe^2)$ is the phospho-sulpho-nitrate of iron.

The salt $((CSOSe)''K^2)$ is the sulphoxyseleniocarbonate of potassium.

## SOLUBILITY.

Certain solid bodies have the property of passing into the liquid state when they are mixed with other bodies which are already in this state, and to remain intimately mixed with these latter substances. Then we say that the solids are soluble in these liquids, and this property which they possess is called solubility.

Examples of solubility are numerous. Sugar is soluble in water, fat is soluble in spirit of turpentine, etc.

When a solid is dissolved in a liquid, sometimes an increase, and at others a decrease of temperature is observed: occasionally the temperature remains unchanged.

These phenomena are thus explained:

Every body in passing from the solid to the liquid state absorbs a certain quantity of heat, and consequently lowers the external temperature. Hence it is evident that in every solution the temperature of the solvent ought to be lowered; further, as all bodies do not require the same quantity of heat to change their state, it is equally evident that the cold produced by the solution ought to present an intensity varying according to the nature of the body dissolved.

This would always be the case if no other phenomena interfered; but the body which is dissolved may exercise a chemical action on the solvent, so that an elevation of temperature is produced and counterbalances in different degrees the cold resulting from the liquefaction. The result observed will depend upon the difference between the two. We have cold in the case where the heat developed by the combination is less than the cold produced by the solution, and heat when the reverse takes place. But the temperature will not vary if the two effects exactly compensate.

The laws which regulate the solubility of bodies are far from being exactly known: besides the general rules there are also exceptions.

First Law.—At the same temperature, the quantity of a solid body which a liquid can dissolve is limited. When a liquid has dissolved all that it can of a body at a given temperature, it is called saturated. Solutions, like ordinary combinations, therefore take place in definite proportions.

Second Law.—When a liquid is saturated with one body it can still dissolve another; often even the solubility of one is augmented by the presence of the other. This latter phenomenon ought to be attributed to the production of new compounds formed by the double decomposition of the two primitive bodies.

Third Law.—The solubility of bodies generally augments with the temperature: 100 parts of water at 10° dissolve 10 parts of nitrate of barium, and 36 parts of the same salt at 100°. Nevertheless, this law is not constant. Besides, the increase of solubility for the same increase of temperature is far from being the same for all bodies; there are some which are more soluble in cold than hot liquids, sulphate of thorium among the number; and there are others which present still greater irregularities. Sulphate of sodium is soluble in water, and its solubility increases as the temperature rises up to +33°. But as the temperature is elevated above 33°, the solubility of the salt decreases.

To explain this curious fact, we suppose the salt which is dissolved between 0° and 33° to be combined with a certain quantity of water, while at 33° this combination is destroyed, leaving the salt anhydrous. To explain this anomaly, we may suppose that the hydrated salt obeys the general law, and that, on the contrary, the solubility of the anhydrous salt decreases with the temperature. Unfortunately, this explanation is quite hypothetical.

Fourth Law.—Bodies, when they are dissolved in liquids, always raise the boiling point of the latter. The amount which they raise it varies with the bodies. It is probably in proportion to the combining power which the liquid has for the solid molecule.

The following table indicates the number of degrees by which the boiling point of water is raised by a weight of different bodies capable of saturating it at the temperature at which it boils under their influence:

| Names of Bodies. | Proportion of Bodies to 100 of Water. | Boiling Points. |
|---|---|---|
| Chloride of barium . . . . . | 60·1 | 104°·3 |
| Chloride of sodium . . . . . | 41·2 | 108°·3 |
| Chloride of ammonium . . . . | 88·9 | 114°·2 |
| Chloride of strontium . . . . . | 117·5 | 117°·8 |
| Nitrate of sodium . . . . . | 224·8 | 121°·0 |
| Nitrate of calcium. . . . . . | 362·0 | 151°·0 |
| Chloride of calcium . . . . . | 325·0 | 179°·0 |

As the solubility of each body varies with the temperature, lines have been constructed called curves of solubility, intended to show at what degree of the thermometer this takes place. The following is the principle of these curves.

Take two lines perpendicular (see fig. 10) to one another. The

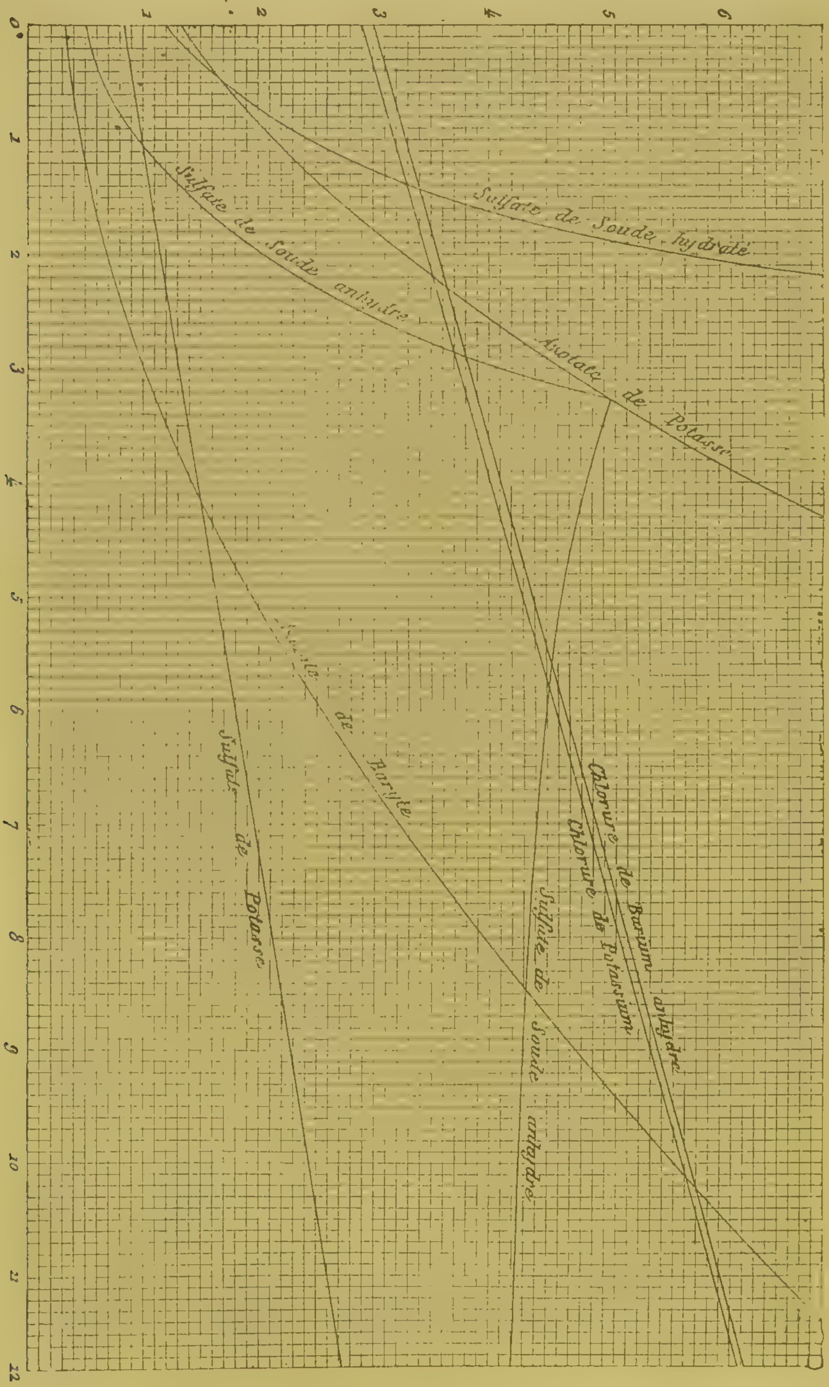

Fig. 10.

horizontal line is divided into a certain number of equal parts, of which each represents 1° of the centigrade thermometer. The vertical line is divided into equal parts, which are not necessarily equal to those of the horizontal line.

If we wish to determine the curve of solubility of a body, we find by experiment what are the quantities of this body dissolved in 100 parts of the solvent at different temperatures.

This done, from the divisions which indicate these temperatures we raise perpendiculars to the horizontal line; then on the vertical line we take the lengths proportional to the quantities of the body dissolved at the different temperatures for which the determination of the solubility has been made. From each of the points thus traced on the vertical line we raise perpendiculars, which meet those raised from the horizontal line. Finally, we join all the points of intersection by a continuous curve, which is the curve of solubility sought for.

From ten to twenty experiments will be enough for the curve to represent the solubility at all degrees of the thermometer with sufficient exactitude.

When we wish, by the help of this curve, to learn the solubility of a body at any temperature, we raise a perpendicular from the point of the horizontal line where this temperature is inscribed. This perpendicular cuts the curve of solubility at a certain point, which we connect with the vertical line. The length of this latter line between the point of connection and the horizontal line represents the quantity of the body capable of being dissolved at the temperature.

The important point, therefore, is to be able to determine exactly the solubility of a body. Two methods can be employed to attain this end.

First Method.—This consists in evaporating with care a known weight P of a solution saturated at a certain temperature, and weighing the dried residue; let the weight be P′; P − P′ will represent the weight of the water evaporated. A simple proportion then gives the quantity of the soluble body which 100 parts of water would dissolve at the same temperature. We have then

$$P - P' : P' :: 100 : x; \text{ that is to say, } x = \frac{100 \times P'}{P - P'}.$$

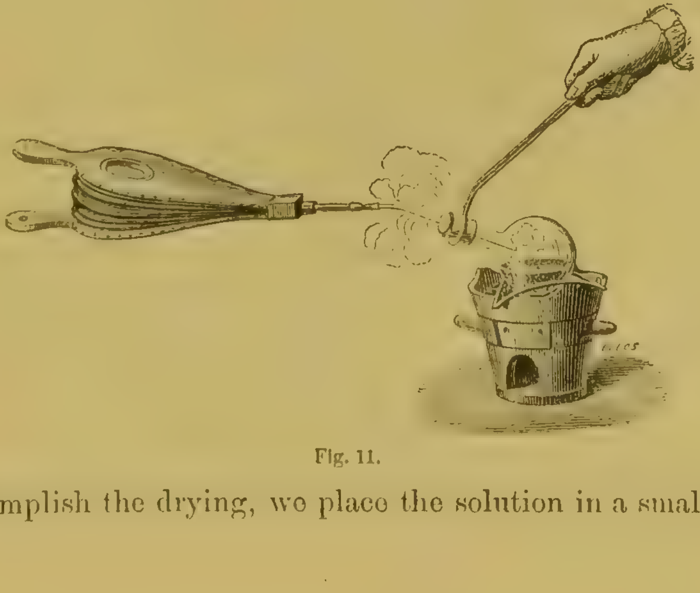

Fig. 11.

To accomplish the drying, we place the solution in a small receiver (fig. 11), which is heated by charcoal. At the end of the operation, to remove the last traces of moisture, we inject dry air into the receiver by the help of a small glass tube adapted to the point of a pair of bellows by means of an india-rubber tube. The receiver must always be held obliquely to prevent the liquid spurting out.

SECOND METHOD.—Instead of evaporating the solution after having weighed it, a re-agent is added capable of precipitating the body dissolved, or, at least, some of its elements. The precipitate is collected, washed, dried, and weighed; and from its weight that of the body which was in solution is deduced.

For example, to determine the solubility of bromide of sodium, we add nitrate of silver to the solution of this salt; and, after having collected it on a filter, washed and dried it, we weigh the bromide of silver which is precipitated; let P be its weight. As we know that 188 parts of bromide of silver contain 80 parts of bromine, we know the weight of bromine contained in P of bromide of silver by the help of proportion:

$$188 : 80 :: \mathrm{P} : x; \text{ that is to say, } x = \frac{80 \times \mathrm{P}}{188} = \mathrm{B},$$

calling B the value of $x$ supposed to be found.

We know that 80 of bromine unite with 23 of sodium, giving 103 of bromide of sodium; then we shall have the quantity of bromide of sodium contained in the solution by means of the proportion—

$$80 : 103 :: \mathrm{B} : x; \text{ that is to say, } x = \frac{103 \times \mathrm{B}}{80}.$$

The weight of bromide of sodium being known, we make the calculation as before.

This proceeding is only applicable when the bodies whose solubility we wish to determine are decomposable by heat.

Whatever may be the method employed, the principal part of the operation is to obtain a saturated solution. We can do this in two different ways.

The most simple and at the same time the most certain way consists in placing in the liquid an excess of the body to be dissolved, and leaving it for a sufficient length of time at the proper temperature.

The second means is only applicable to bodies which, according to the general rule, are rendered more soluble by heat. It consists in saturating the liquid at a temperature higher than that at which we wish to make the experiment, and then leaving it to become cold. The excess of the body dissolved is deposited, and when the thermometer marks the degree required, the saturated solution is decanted.

This proceeding is liable to error. Sometimes it happens that, when the temperature becomes lowered, the excess of the soluble body which ought to be deposited is not; then the liquid contains in solution a quantity of this body greater than that which it would have taken up if the solution had been made at once at this temperature. Nevertheless, it is generally sufficient in this case to shake the solution, when the excess of the body dissolved becomes crystallized. Solutions which are in the above condition are said to be super-saturated.

To obtain them it is necessary to keep them from contact with air while they are cooling. This can be done either by enclosing them in a tube hermetically sealed, or by covering them with a coating of oil, or by simply placing them under a bell-glass. In the first case it is sufficient to break the end of the tube which contains them; and in the second, to agitate the liquid with a glass rod, to bring about the crystallization.

The experiment succeeds very well with sulphate of sodium. We pour into a glass tube a solution of this salt, saturated while hot, taking care to fill about $\frac{7}{8}$ of the tube; we then boil the liquid to remove the air, and during the boiling we hermetically close the contracted part. Then we can let the apparatus (fig. 12) cool without the sulphate of sodium becoming crystallized; but if we break the end of the tube crystallization takes place immediately, and the liquid becomes a solid mass.

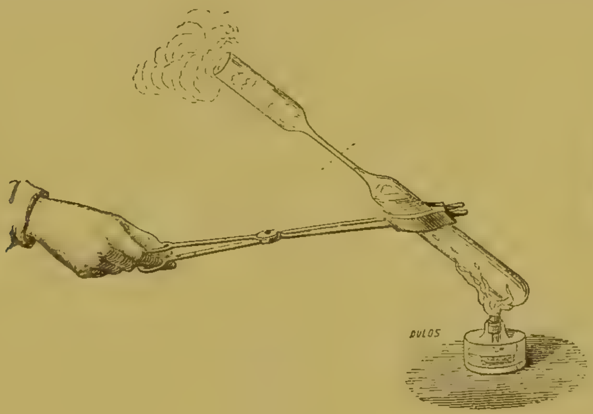

Fig. 12.

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When a super-saturated solution has been obtained by protecting it from the air either by means of a coating of oil or by a bell-glass, certain curious phenomena are observed: thus, if a glass rod be placed in such a solution, it instantly crystallizes. The rod loses its property when hot, or if after being heated it is protected from the air while cooling.

If a current of ordinary air be made to pass through a super-saturated solution, crystallization takes place immediately. But the air will no longer produce the crystallization if, before passing into the solution, it goes through a hot tube, or traverses a series of empty U-shaped tubes, or be sifted by passing through cotton.

These facts seem extraordinary at first sight, but are very easily explained.

The crystallization of super-saturated solutions is owing to the solid particles which become deposited on the objects exposed to the air, or which the air holds in suspension. Moreover, it has been shown that, in order that powders may possess this property, they must contain traces of the matter that constitutes the super-saturated solution. These solutions are the most sensitive re-agents imaginable for determining whether air contains the bodies of which they are composed or not.

When the air is sifted or made to pass through the series of tubes, it is deprived of its powders, and when it is heated, those powders which might produce crystallization lose their crystalline form, and with it their power of serving as nuclei for crystals.

**Solubility of Gases.**—The laws we have just studied apply to the solubility of solids, but not to the solubility of gases. When a liquid dissolves a solid, the affinity between the two substances alone determines the change of state of the solid, and as this change requires caloric, heat favours the solution.

When it is a gas that is dissolved, the affinity of the liquid for the gas again determines the change of state, but in inverse order. This new change of state, instead of being accompanied by an absorption of heat, is accompanied by its disengagement. It is evident from this that, if it be heated, an effect will be produced the reverse of that which results from the affinity of the two bodies; that is to say, the solution will be destroyed. What reasoning would lead us to expect, experiment demonstrates. The quantities of gas dissolved in a liquid decrease with the elevation of the temperature; and when this becomes sufficiently high, the whole of the gas again becomes free.

On the other hand, when we compress gases, we bring their molecules nearer together, and the increase of the attractive force which acts between them, is the result. In compressing gases, the same effect is produced as if they were cooled. This is so true, that we can liquefy gases by pressure alone.

We thence conclude that pressure, like reduction of temperature, ought to favour the solution of gases, and here again reasoning is confirmed by experiment.

Gases, in fact, dissolve in proportion to the pressure. When this becomes two, three, or four times greater, the weight of gas dissolved also becomes two, three, or four times greater.

We can explain this principle by saying that a liquid at a given temperature always dissolves the same *volume* of a gas, whatever may be the pressure. As the weight of a volume of gas is in proportion to the pressure which it supports, it is evident that the two expressions are the same.

In Seltzer water we have an example of the action of pressure on the solubility of gases. This water has been saturated with carbonic anhydride under a pressure of 5 atmospheres. When we place it in communication with the ordinary atmosphere, the pressure diminishing $\frac{4}{5}$, $\frac{4}{5}$ of the gas dissolved is disengaged, and produces considerable effervescence.

Let us see what occurs when a liquid acts not on a single gas, but on a mixture of several gases.

Let there be a mixture of two gases A and B, of which A forms $\frac{1}{5}$ and B $\frac{4}{5}$; if, the volume remaining the same, the gas B were to disappear, the gas A would occupy all the space, and would consequently have a pressure 5 times less than that of the original mixture. It would then be capable of being dissolved in proportion to this pressure. Let us call the quantity which would become dissolved P.

If the gas A disappeared, B would occupy the space and would have a pressure which would be the $\frac{4}{5}$ of that of the mixture. It could be dissolved in proportion to this pressure. Let P′ be the quantity which would become dissolved.

We know that when the two gases are mixed, the respective quantities of A and B which are dissolved are equal to P and to P′.

We explain this by saying: when a liquid acts on a mixture of several gases, it dissolves of each of them that quantity which would be dissolved if this gas were alone in the mixture, with that pressure which belongs to it.

## WATER OF INTERPOSITION—WATER OF CRYSTALLIZATION—WATER OF CONSTITUTION.

When a body crystallizes, it sometimes happens that the crystals placed over one another contain a certain quantity of the mother liquor (the solution in which the crystals were formed). In this case, the water enclosed presents no constant relation with the crystal. It is found in the state of a simple mixture, and is called *water of interposition.*

On the contrary, many crystals contain water in definite proportions and in the state of real combination. This combined water bears the name of *water of crystallization.*

The same body can crystallize with different proportions of water, according to the conditions under which the crystals are formed; thus, sulphate of magnesium crystallized at the ordinary temperature retains 7 molecules of water and answers to the formula—

$$\left.\begin{matrix}SO^{2''}\\Mg\end{matrix}\right\}O^2 + 7\text{ aq.}$$

in which aq. represents a molecule of water of crystallization. The same salt precipitates from its solution below 0° with 12 molecules of water and answers to the formula—

$$\left.\begin{matrix}SO^{2''}\\Mg\end{matrix}\right\}O^2 + 12\text{ aq.}$$

Water of crystallization does not seem to act any important part in the constitution of the body with which it is united. When it is driven off by the application of heat, on redissolving, the body can again be crystallized, and will then regain all the water that it lost. In this case we observe that none of its physical or chemical properties have been modified.

This water, on the contrary, has a very important influence on the form of the crystal; if it be driven off by evaporation, the crystal is destroyed.

Bodies which contain water of crystallization, and whose solubility increases with the temperature, sometimes give rise to a singular phenomenon. When they are heated, they dissolve in their water of crystallization, and seem to melt; if we continue the application of heat, the water evaporates, and the body regains the solid state. It is only at a much higher temperature that the body really melts. This apparent fusion has received the name of *aqueous* fusion, in opposition to the real fusion, which is called *igneous.*

There are crystals which may wholly or partly lose their water of crystallization by simple exposure to the air, and which at the same time fall to powder; they are called efflorescent. Sulphate of sodium has this property in a very high degree.

Other bodies, on the contrary, have such affinity for water that they seize upon that which the atmosphere contains in the state of vapour; these are called deliquescent. Carbonate of potassium is among the number; on leaving it for several days in contact with the air, instead of a solid body we find a syrupy solution.

It has been asked whether the water exists in crystals in the liquid or in the solid state. The specific heat of ice differing from that of water, enables us to solve the problem.

We know that the quantity of heat necessary to raise 1° the temperature of a compound, is equal to the sum of the quantities which each of its components absorbs. If, therefore, we call $M, M', M''$ the masses of three bodies, and $C, C', C''$ their specific heat, the quantity of heat capable of raising 1° $M + M' + M''$ will be $MC + M'C' + M''C''$. The quantity of heat which will raise the united weights of the compound 1°, that is to say, the specific heat of this latter, will be

$$\frac{MC + M'C' + M''C''}{M + M' + M''}.$$

Hydrated crystals have a capacity for heat which is represented by $\frac{MC + M'C'}{M + M'}$, representing by $M$ and $M'$, $C$ and $C'$ the masses and the capacities for heat respectively of the anhydrous body and the water, always making $C'$ equal to the specific heat of ice. It is therefore in the solid state that water exists in crystals.

To determine the proportion of water of crystallization which crystals contain, we weigh a certain quantity of the crystals reduced to powder; let $P$ be its weight. Then we place it in a stove heated to 100° by boiling water, or by oil to 120°, 140°, 200°, etc., according to the facility with which it becomes dehydrated. We prolong the action of heat until two successive weighings indicate no further loss of weight; let P′ be the weight of the dried matter, P − P′ represents the water of crystallization. Knowing these numbers, we can determine, by proportion, the weight of the water which is combined with a molecule of the anhydrous body. Q being the molecular weight of the body, then, $P : P - P' :: Q : x$; therefore $x = \frac{Q \times (P - P')}{P}$. On dividing $x$ by the molecular weight of the water, that is to say by 18, we learn what is the number of molecules of water combined with a molecule of the body, and then arrive at the formula of the crystal.

Sometimes bodies lose water under the influence of heat, and crystals sometimes not only lose their water, but become so altered in their properties that, when redissolved in water, they will not regain their primitive characters.

The formula of citric acid crystallized in the cold is $C^6H^8O^7 + aq.$ At 100° it loses its water of crystallization; but if it be heated more strongly, it will also lose a molecule of water. Then its formula becomes $C^6H^6O^6$.

The dehydrated compound constitutes a new acid, aconitic acid, entirely different from citric acid, and incapable of reconstituting this latter under the influence of water.

The water whose elimination determines a change in the nature of bodies is called *water of constitution.* Does it exist ready formed in the molecules of the compounds which lose it? We do not know; but it is probable that it is formed at the time the crystal is heated, by the union of a part of the hydrogen with a part of the oxygen which it contains. It is believed that the action of heat may produce a similar modification in a complex molecule, and to explain the phenomenon it is not necessary to admit that the water exists ready formed in the molecules in question.

## POLYMORPHISM—ALLOTROPY—ISOMERISM.

Nothing is less easy than to define these three words and to determine exactly their respective acceptations.

There exists a vast series of phenomena, of which polymorphism constitutes the first term, allotropy the intermediate, and isomerism the extreme term. Now when we divide a series into several parts, we assign to each certain distinctive characters taken from their medium terms; as to the extreme terms, they always participate in the properties of the groups which separate them; therefore the groups of which we speak cannot be absolutely distinguished by special characteristics. It is therefore necessary, in order to define polymorphism, allotropy, and isomerism, to give a clear idea of these three expressions, even if we leave out certain facts of which the classification is difficult, an inherent defect in the system of classification.

Solids which crystallize in different conditions sometimes crystallize in two different systems: they are then called polymorphous. Sulphur, which crystallizes from its solution in octahedra of the fourth system, when crystallized by means of fusion forms prisms having a rhombic base, of the fifth system. This is a polymorphous body.

The word polymorphous, created for the differences which are presented by bodies in their crystallization, has received a greater extension. M. Dumas has applied it to the changes of colouring and consistence which are produced by the action of heat.

We can thence define polymorphism: *The faculty possessed by bodies chemically identical, of having physical properties differing according to the conditions in which they are placed.*

Again, a body placed in different conditions may undergo modifications in its physical and also in its chemical properties; in this case we have the phenomena of allotropy or isomerism.

These two latter terms are nevertheless far from being synonymous.

After having carefully studied the different acceptations in which these two words have been taken, I am convinced that chemists have instinctively designated under the name of allotropy, cases in which, although the body possesses different chemical properties, we can prove that it is always the same body modified.

On the contrary, we call isomeric, bodies entirely distinct, but having the same qualitative and quantitative composition.

Thus phosphorus being heated, changes its properties, as we have already had occasion to show; this change even affects its chemical properties. If we heat it still further, the phosphorus regains its original properties. Phosphorus can therefore exist in two different states, but it is always phosphorus. This is a phenomenon of allotropy.

Let us now compare the formiate of ethyl $C^3H^6O^2$ with acetate of methyl $C^3H^6O^2$. These two bodies have the same composition, but they can never be transformed one into the other; more, if we destroy their molecules by means of the same re-agents, the products we obtain are quite different. Formiate of ethyl and acetate of methyl are two perfectly distinct bodies; two isomeric bodies.

Chemists have felt, without having determined, that herein lies the difference which exists between allotropy and isomerism. When they wish to designate facts of allotropy, they give to the bodies in which they are observed an invariable name, and say that it assumes several states, while they give perfectly distinct names to isomeric bodies.

Two names are not given to sulphur, to phosphorus, to per-hydrate of iron; we say that each of these bodies exists under two distinct allotropic states, but we designate by different names formiate of ethyl and acetate of methyl; aldehyd and oxide of ethylene also, which have each the formula $C^2H^4O$, etc.

An example taken from natural history will illustrate my idea: allotropy only makes races; isomerism creates distinct *species.*

To sum up, we ought to understand by allotropy:

*The property in virtue of which the same body can have different chemical characters.*

And by isomerism:

*The fact that different bodies may present an identical qualitative and quantitative composition.*

Originally, the word allotropy was only applied to elements, later it was also applied to some compounds; we will apply it to all bodies, but keep ourselves within the limits of preceding definitions. Certain reputed isomeric compounds will therefore only be in our view allotropic modifications of one and the same body; we will only give one example: tartaric acid which turns the plane of polarization of light to the right, tartaric acid which turns it to the left, and that which does not deviate it at all, are not in our eyes three isomeric compounds, but the same compound which assumes several allotropic states.

Isomeric bodies may present between themselves relations of different composition; thence the several classes of *isomerides*.

These classes, according to M. Berthelot, are five in number; but we will only retain four, because in the fifth, under the name of *physical* isomerism, M. Berthelot places that which is generally called allotropy.

First Class.—This contains bodies which have no other relation than their identity of composition, without our being able to observe the least analogy in their metamorphoses. Their molecules correspond to formulas, sometimes identical, and sometimes multiples the one of the others.

*These bodies are isomeric by equivalent composition.*—We will take for example aldehyd and oxide of ethylene, of which the common formula is ($C^2H^4O$); lactide and acrylic acid, which both have for formula ($C^3H^4O^2$); lactic acid, which answers to the formula ($C^3H^6O^3$); and glucose ($C^6H^{12}O^6$), double the preceding one.

Second Class.—Here we find compounds formed by the union of different components, but presenting such relations to each other that by the act of combination a species of compensation is established; one of the generators of one isomeric body possessing most what the other possesses least, relatively to the generators of the other isomeric body.

*These are isomerides by metamerism.*—The facts of this order are numerous. Formiate of ethyl and acetate of methyl furnish us an example. In formiate of ethyl $\left(\left.\begin{matrix}CHO\\ \hline C^2H^5\end{matrix}\right\}O\right)$, the acid radicle (CHO) contains an atom of carbon and two atoms of hydrogen less than the acid radicle ($C^2H^3O$) of acetate of methyl $\left(\left.\begin{matrix}C^2H^3O\\ CH^3\end{matrix}\right\}O\right)$; but, on the other hand, the radicle methyl ($CH^3$), which is in the second of these bodies, contains $CH^2$ less than the radicle ethyl ($C^2H^5$) which acts in the first. To sum up, the two compounds contain therefore the same number of atoms of each component element.

Third Class.—This contains an entire group of substances of which the properties are alike and the centesimal composition identical, but of which the molecular composition is different; the molecular weight of one being a multiple of the molecular weight of others.

*These are isomerides by polymerism.*—As an example we give: ethylene ($C^2H^4$), propylene ($C^3H^6$), butylene ($C^4H^8$).

FOURTH CLASS.—In this are classed bodies which have the same centesimal composition and the same formula, and which moreover present the same general system of reactions; but which remain distinct by a certain number of physical and chemical properties which they retain, or at least some of them, in passing through their combinations.

*These are isomerides properly so called.*—Cresylic phenol and benzilic alcohol, which have the formula ($C^7H^8O$); toluic acid and alpha-toluic acid, whose formula is ($C^8H^8O^2$), belong to this class.*

## CLASSIFICATION OF BODIES.

As we have already had occasion to say, simple bodies have been classed in such a series that each body therein is electro-positive relatively to the elements which precede it, and electro-negative towards those which follow.

As this series neither indicates the analogies nor the differences of properties which the bodies present, we cannot rationally apply it to their study.

Bodies have been also divided into metalloids and metals, and then each of these classes subdivided. The characters which serve to establish this division are far from being sufficient.

The only natural classification would consist in making several families of all the simple bodies, each of which families should contain those bodies which have the same atomicity. Then the bodies should be arranged in each family on the principle of the electric series.

Thus the first family would contain monatomic bodies: fluorine, chlorine, bromine, iodine, hydrogen, silver, lithium, sodium, potassium, rubidium, cæsium, and perhaps thallium whose place is not yet quite determined. Each of these bodies is electro-negative to those which follow and electro-positive to those which precede it.

We will, however, confine ourselves to that classification which divides bodies into metalloids and metals, and will only add to the former certain elements up to this time reputed metals, and which, according to the researches of M. Marignac, cannot be separated from silicon. In making any further subdivisions, we will take as basis the atomicity of bodies. Nevertheless several exceptions to this general rule will be necessary, and sometimes we shall have to classify certain bodies, not by their absolute atomicity, but according to their most ordinary quantivalence. We shall do this whenever the absolute atomicity is only manifested in rare cases, as takes place with oxygen, sulphur, selenium and tellurium, which are in reality tetratomic, but which nearly always act as bivalents, and with iodine, which in most cases acts as monovalent, though it is triatomic.

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* To these different classes of isomerism M. Berthelot adds *Kenomerism, or isomerism of bodies formed by the elimination of different or identical elements at the cost of distinct compounds.* Thus aldehyd and oxide of ethylene, which have both for formula ($C^2H^4O$), and which are derived, the first from alcohol ($C^2H^6O$), by elimination of $H^2$, and the second from glycol ($C^2H^6O^2$), by elimination of $H^2O$, would be kenomeric bodies. We have not retained this class of isomerism, which is only based on the constitution of bodies, and the creation of which seems to us to be arbitrary.

The following table shows the differences which distinguish metalloids from metals:—

| METALLOIDS. | METALS. |
|---|---|
| 1. Several metalloids are gaseous. | 1. There is no gaseous metal. |
| 2. Metalloids have not the lustre called metallic. | 2. Metals possess metallic lustre. |
| 3. Metalloids are bad conductors of heat and electricity. | 3. Metals are good conductors of electricity and heat. |
| 4. Metalloids have a density relatively low. | 4. Metals have a density relatively high. |
| 5. Oxides of metalloids, on combining with water, ordinarily produce acids, seldom bases. | 5. Oxides of metals, on combining with water, produce bases, seldom acids. |
| 6. Metalloids are always electro-negative in the compounds which they form on uniting with metals. | 6. Metals are always electro-positive in the compounds which they form on uniting with metalloids. |

**Subdivision of Metalloids.**—We will divide the metalloids into five natural groups, our classification being that of M. Dumas, slightly modified.

FIRST GROUP.—Contains monatomic metalloids; they are: chlorine, bromine, iodine, fluorine, and hydrogen.

SECOND GROUP.—Contains biatomic metalloids; which are: oxygen, sulphur, selenium, and tellurium.

THIRD GROUP.—At present only contains one metalloid, boron, which is triatomic.

FOURTH GROUP.—In this we classify the tetratomic metalloids: silicon, Carb
zirconium, titanium, tin, and thorium.

FIFTH GROUP.—This contains the pentatomic metalloids, which are: nitrogen, phosphorus, arsenic, antimony, bismuth, uranium, tantalium and niobium.

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# PART SECOND.

## SIMPLE BODIES AND THEIR PRINCIPAL COMPOUNDS.

# METALLOIDS.

## FIRST GROUP (MONATOMIC METALLOIDS).

### CHLORINE $\left.\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right\}$

Atomic weight = 35·5. Molecular weight = 71.

Chlorine may be obtained either by heating binoxide of manganese with hydrochloric acid, or by heating the same oxide with a mixture of sulphuric acid and chloride of sodium.

First Process.

$$\underset{\text{Binoxide of manganese.}}{\left(\mathrm{MnO^2}\right)} + \underset{\text{Hydrochloric acid.}}{4\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{Cl}\end{matrix}\right\}\right)} = \underset{\text{Chloride of manganese.}}{\left(\left.\begin{matrix}\mathrm{Mn''}\\\mathrm{Cl^2}\end{matrix}\right\}\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Free Chlorine.}}{\left.\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right\}}$$

Second Process.

$$\underset{\text{Binoxide of manganese.}}{\left(\mathrm{MnO^2}\right)} + \underset{\text{Sulphuric acid.}}{2\left(\left.\begin{matrix}\mathrm{SO^{2''}}\\\mathrm{H^2}\end{matrix}\right\}\mathrm{O^2}\right)} + \underset{\text{Chloride of sodium.}}{2\left(\left.\begin{matrix}\mathrm{Na}\\\mathrm{Cl}\end{matrix}\right\}\right)} =$$

$$\underset{\text{Sulphate of manganese.}}{\left(\left.\begin{matrix}\mathrm{SO^{2''}}\\\mathrm{Mn''}\end{matrix}\right\}\mathrm{O^2}\right)} + \underset{\text{Sulphate of sodium.}}{\left(\left.\begin{matrix}\mathrm{SO^{2''}}\\\mathrm{Na^2}\end{matrix}\right\}\mathrm{O^2}\right)} + \underset{\text{Free Chlorine.}}{\left.\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right\}} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}$$

Chlorine is gaseous under ordinary conditions. It becomes liquefied under a pressure of five atmospheres; its colour is a greenish yellow; its density in the gaseous state is 2·44, and in the liquid state 1·33. Owing to its great density, if gaseous chlorine be disengaged in a tube terminating at the bottom of a vase, the air will be gradually displaced and the vase filled with pure chlorine.

Chlorine dissolves in about the third of its volume of water. To obtain a saturated solution we use Woulfe's apparatus (fig. 13). This consists of a series of bottles, C, D, E, F; each bottle having three tubes: the first, placed in the middle, goes to the bottom of the vessel, and its top terminates in a funnel, for the purpose of introducing water. Moreover, if, in consequence of the temperature being lowered, the pressure diminishes in one vessel, the liquid of the next would have a tendency to rise through one of the lateral tubes, and to pass into the first bottle. The tube in the centre prevents this accident: when the gas becomes rarefied in one vessel, the air enters by this tube, and the pressure is re-established. The middle one, for this reason, is called the safety tube. The two others pass through necks at each side. The first, plunged to the bottom of the liquid, brings the gas to be dissolved; the other stops just below the neck, and consequently does not touch the liquid, so that it may furnish a free passage for the gas which has not been dissolved to pass on to the succeeding bottles.

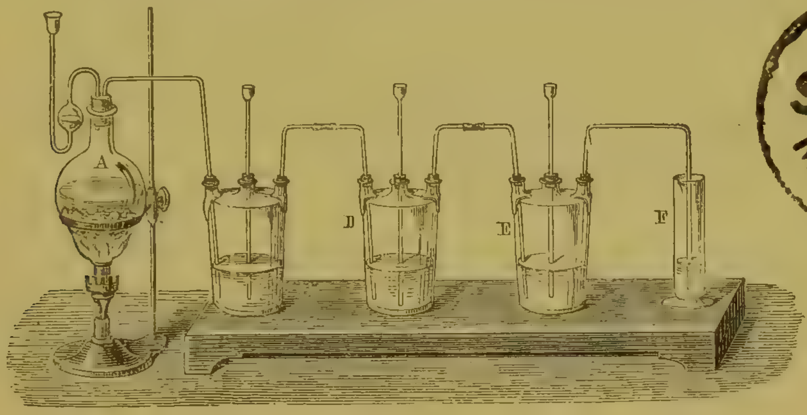

Fig. 13.

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In the case of chlorine, the tube which terminates the apparatus should pass into a vessel containing milk of lime, to absorb the excess of chlorine and to prevent its irritating effects.

When a solution of chlorine is cooled to 0° crystals are obtained which contain 28 parts of chlorine and 72 of water, which nearly corresponds to the formula $Cl^2 . 10H^2O$. These crystals, enclosed in a tube hermetically sealed, decompose when heated, and the gas set free, which is developed in too large a quantity to be dissolved in the water, is compressed to liquefaction. Then the tube contains two strata: one, liquid chlorine; the other, water saturated with this metalloid.

Chlorine combines directly with hydrogen under the influence of light; when the mixture is submitted to sunlight the reaction is instantaneous, and an explosion is the consequence; in diffused light, on the contrary, it requires rather a long time. In total darkness the combination does not take place unless chlorine which has been previously exposed to sunlight (insolated) be employed: in the latter case it is equally instantaneous. Insolated chlorine also differs from ordinary chlorine by other properties. It disengages more heat in reacting on potash; and even when the solutions of this base are largely diluted it forms chlorate of potassium, which would not occur with normal chlorine. Insolated chlorine is, therefore, an allotropic state of chlorine.

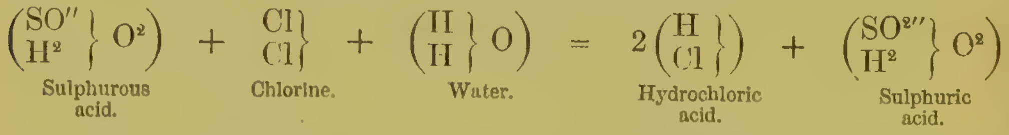
Chlorine combines directly with most metals, and particularly with mercury, and this prevents it from being collected over that liquid.

Arsenic and antimony take fire spontaneously when they are placed in a vessel filled with chlorine. Copper also burns when it is previously heated. Phosphorus inflames in it spontaneously.

If chlorine and aqueous vapour be passed into a tube of porcelain red hot, the water is decomposed, oxygen is set free, and hydrochloric acid is formed; in the cold, and under the influence of light, the solution of chlorine undergoes in time a similar decomposition.

In presence of water chlorine acts as an energetic oxydizer; it appropriates hydrogen, and sets oxygen free, which, in the nascent state, has very strong affinities.

By this means we can easily transform sulphurous into sulphuric acid.



$$\underset{\text{Sulphurous acid.}}{\left(\left.\begin{matrix}SO''\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Chlorine.}}{\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)}$$

Chlorine, by acting on organic substances, modifies them greatly, on account of its affinity for the hydrogen which these substances contain. It destroys colouring principles and miasmata. These two properties are utilized. In trade its decolorizing action is applied for bleaching linen and cotton goods. In medicine it is used as a disinfectant.

## BROMINE $\left.\begin{matrix}Br\\Br\end{matrix}\right\}$

**Atomic weight = 80. Molecular weight = 160.**

Bromine is obtained by a process analogous to that used for chlorine; viz., by heating a mixture of bromide of sodium, peroxide of manganese, and sulphuric acid. The vapour is collected in a cold receiver. As bromine acts strongly on cork, it is necessary to use apparatus in which all the pieces are ground to fit exactly.

Bromine is liquid at the ordinary temperature. Its colour is a deep reddish brown; at — 20° it becomes solid, and forms grey laminæ; about 47° it is converted into a yellowish vapour.

The density of liquid bromine is 2·97, and of bromine vapour 5·39.

The odour of this body is very irritating, and strongly affects the organs of respiration.

Bromine combines with water at 0°, forming a crystalline hydrate. This hydrate is decomposed at 15° or 20°.

The affinities of bromine are of the same nature as those of chlorine, but it combines with oxygen with greater energy, while with all other bodies it combines with less energy. The result is that chlorine displaces bromine in all the compounds the latter forms, excepting with oxygen, and that bromine displaces chlorine from its oxygenized compounds.

### COMBINATION OF CHLORINE WITH BROMINE.

We only know one chloride of bromine which has not been well studied. It is formed by passing chlorine gas through liquid bromine.

## IODINE $\left.\begin{matrix}I\\I\end{matrix}\right\}$

Atomic weight = 127. Molecular weight = 254.

This metalloid can be obtained either by decomposing a solution of iodide of sodium by a current of chlorine, and collecting on a filter the iodine which is precipitated, or by the same reaction as chlorine and bromine, substituting a metallic iodide for the chlorides and bromides.

Iodine is solid, crystallizing in greyish scales, which have a metallic lustre. It melts at 107° and boils at 180°. Its vapours have a beautiful violet colour. The odour of iodine is something like that of chlorine, but is much fainter, and can be better tolerated.

Pure water only dissolves $\frac{1}{7000}$ of its weight, but it dissolves considerable quantities when it contains in solution either iodides or hydriodic acid. Alcohol, ether, benzine, chloroform, and the essences dissolve iodine readily.

The density of iodine is 4·95; its vapour density 8·716. Iodine stains paper and the skin brown; but the discoloration is not permanent.

The smallest quantity of iodine colours starch paste a beautiful blue. The colour fades away if the solution be heated, and the liquid regains its colour on cooling.

The affinities of iodine are of the same nature as those of chlorine and bromine, but it has a stronger affinity for oxygen than these bodies, and a weaker affinity for all other elements. The result is that, while chlorine and bromine displace it from all its non-oxygenized combinations, it displaces them from their oxygenized compounds.

Iodine is a much-used and valuable medicine; it cures goître when this is merely owing to hypertrophy of the thyroid body; above all, it prevents this affection from developing itself. It is advisable to mix iodine compounds with the food in places where goître is endemic.

Iodine succeeds also in scrofula and in tertiary syphilis. M. Piorry is said to have obtained excellent results with it in pulmonary consumption.

### COMBINATIONS OF IODINE WITH CHLORINE AND BROMINE.

**Chlorides of Iodine.**—Two chlorides of iodine are known: one protochloride ($ICl$), and a perchloride ($ICl^3$). These two chlorides are obtained by making chlorine act directly on iodine. The chlorine must be in excess if we want to obtain perchloride, and the iodine, if it is the protochloride we wish to prepare.

Protochloride of iodine is liquid, and perchloride solid. They both, in presence of a great quantity of water and an excess of chlorine, generate iodic and hydrochloric acids.

**Bromides of Iodine.**—On combining directly bromine with iodine we obtain, according to the respective quantities of these bodies, either a solid protobromide, or a liquid perbromide.

## FLUORINE $\left\{\begin{matrix}\mathrm{Fl}\\ \mathrm{Fl}\end{matrix}\right.$

Atomic weight = 19. Molecular weight = 38(?)

Fluorine exists in the compounds which are called fluorides, and also in hydrofluoric acid. The facility with which it attacks all bodies has not allowed it as yet to be obtained in a free state.

## HYDROGEN $\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}$

Atomic weight = 1. Molecular weight = 2.

Hydrogen, combined with oxygen, is contained in water.

Free hydrogen can be obtained by passing the vapour of water over iron filings placed in a tube of porcelain heated to redness.

$$\underset{\text{Iron.}}{3\left(\mathrm{Fe}\right)} + \underset{\text{Water.}}{4\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\text{Magnetic oxide of iron.}}{\left(\mathrm{Fe^3O^4}\right)} + \underset{\text{Hydrogen.}}{4\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}}$$

It is, nevertheless, more convenient to displace hydrogen from (cold) diluted sulphuric or hydrochloric acid by a metal, such as iron or zinc.

$$\underset{\text{Zinc.}}{\mathrm{Zn}''} + \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}\mathrm{SO^{2\prime\prime}}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{O^2}\right)} = \underset{\text{Sulphate of zinc.}}{\left(\left.\begin{matrix}\mathrm{SO^{2\prime\prime}}\\ \mathrm{Zn''}\end{matrix}\right\}\mathrm{O^2}\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}}$$

This operation takes place in a flask with two necks (fig. 14). Into one of these is adapted a tube which goes down to the bottom of the liquid, and allows the acid to be poured in; in the other is placed a tube, which merely enters just within the neck, and allows the gas to pass out. A very diluted acid ought always to be employed in this operation, otherwise the sulphate of zinc, not meeting with anything to dissolve it, is deposited on the metal, and preserves it from contact with the acid, and so prevents the process from being continued.

Hydrogen can also be obtained from the decomposition of water by potassium or sodium; a piece of one or the other of these metals is wrapped in paper and introduced under a bell glass placed over mercury, there being a little water in the upper part of the glass. The potassium, owing to its small specific gravity, rises to the top of the fluids; then the water and the mercury become lowered, the potassium (or sodium) disappears, and the bell fills with hydrogen. The reaction which takes place is the following:—

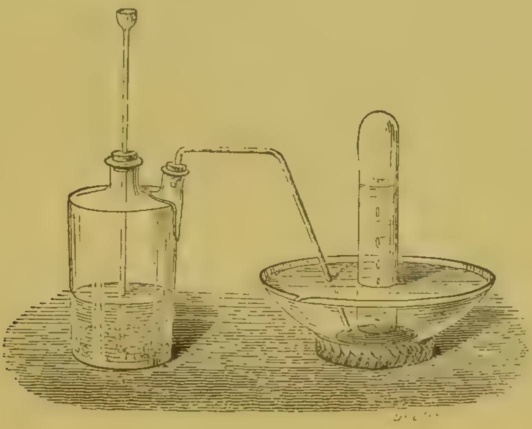


Fig. 14.

$$\underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Potassium.}}{\left.\begin{matrix}K\\K\end{matrix}\right\}} = \underset{\substack{\text{Hydrate of}\\\text{potassium.}}}{2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}}$$

This reaction is too energetic to be employed for the continuous production of hydrogen; but it may be moderated by employing the amalgam of potassium or sodium instead of the pure metal. An apparatus is then used similar to that in which zinc is treated by sulphuric acid.

Finally, hydrogen chemically pure can be obtained by means of the galvanic battery. For this purpose, the apparatus (fig. 15) is employed. It is a glass flask with a hole at the bottom, into which is cemented a wire of platinum *a* covered with a layer of zinc amalgam. The flask is then filled up to the level of the neck S with water acidu-

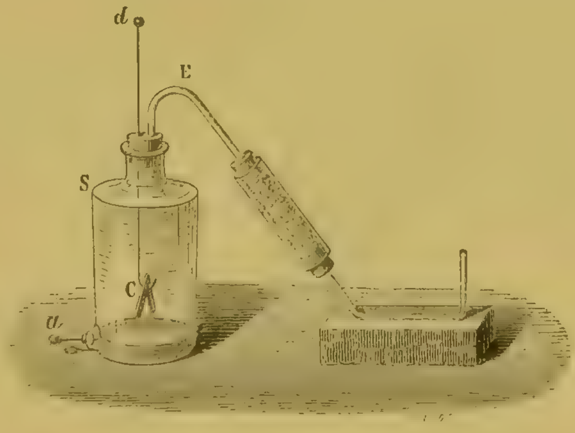


Fig. 15.

lated by pure sulphuric acid. This neck is closed by a stopper through which passes: 1st, a platinum wire *d*; 2nd, a disengagement tube E. In the course of this latter a larger tube is interposed full of chloride of calcium—a substance having a great affinity for moisture—for the purpose of drying the gas. The platinum wire *d* passes into the liquid and is terminated by a hook C, to which is suspended a sheet of the same metal. On placing the wire *d* in communication with the negative pole of a battery of two cells, and the wire *a* in communication with the positive pole of the same battery, pure hydrogen is disengaged at C.

Hydrogen gas has not been liquefied under any pressure or at any temperature. It is colourless, inodorous, and tasteless; its density is 0·0692.

Water dissolves about $\frac{1}{100}$ of its volume. Hydrogen is highly combustible. If it be disengaged through a very slender tube and lighted, it burns with a very hot but not a bright flame; an apparatus made on this principle is called the philosophical lamp. The flame deposits vapour of water on cold bodies, which shows that water is composed of hydrogen and oxygen.

When a glass cylinder, open at both ends, is placed round the flame of hydrogen, a sound is heard which may be made sharper or duller by sinking the cylinder more or less. This is owing to a series of vibrations which take place in the cylinder in consequence of the formation and sudden condensation of a certain quantity of aqueous vapour.

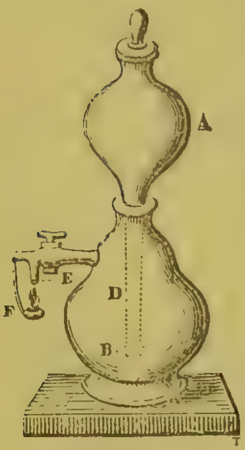


Fig. 16.

Hydrogen, which does not generally ignite in air unless it is brought in contact with an ignited substance, inflames spontaneously under the influence of spongy platinum.* An apparatus has been constructed on this principle by which light is easily obtained, which is called the hydrogen lamp (fig. 16).

This apparatus consists of a lower receiver, which has an opening at the top and one at the side. At the bottom of the interior of this receiver a large hollow cylinder of zinc is placed B. A second receiver A, which has an opening at the top, closed by a ground stopper, and terminating at the lower part by a long tube D open at the end, is placed over the first, so that the open end of the tube which terminates it passes deeply into the zinc cylinder. The upper end of this tube is accurately fitted into the higher opening of the lower receiver.

Finally, this latter receiver has at E a tube with a stopcock, and opposite the opening of this is a sponge of platinum F.

The apparatus acts in the following manner:

If, the stopcock E being open, we pour dilute sulphuric acid into the receiver A, the acid falls by the tube into the lower receiver, and acts on the zinc, on contact with which it gives rise to a disengagement of hydrogen. The gas escapes by the tap E, strikes against the platinum sponge, and ignites. If we wish the apparatus to cease acting, we close the tap E, taking care to keep open the stopper of the vase A; the gas produced in the lower vessel, finding no means of exit, is compressed, it presses on the liquid contained in this vase, and obliges it to rise in the tube D and the receiver A.

---

* We call "spongy" platinum the spongy mass of platinum which is obtained on decomposing certain compounds of this metal by heat.

The zinc and sulphuric acid thus becoming separated, chemical action is arrested. When we again cause the apparatus to act, we merely open the tap E; the pressure of the gas in the lower receiver ceasing at once, the liquid again descends into it and the disengagement of gas recommences.

Therefore, whenever we want a light we have only to open the stopcock. Unfortunately, the platinum sponge soon loses its power of igniting the gas if care be not taken to renew it from time to time by making it red hot. This prevents this apparatus from being employed in domestic use.

A mixture of hydrogen and oxygen explodes when ignited. The most violent explosion is obtained from the mixture of two volumes of hydrogen with one of oxygen. If the two gases be placed in separate gasometers, from which their flow can be regulated, and both made to pass in the above proportions into a tube of very strong metal containing several disks of metallic gauze, the mixture as it comes out of the tube may be lighted without danger. The flame obtained gives a temperature of about 2500°; a similar jet ignited, and directed on to a piece of chalk, renders it incandescent, and produces a bright light, which has been called Drummond's, or the lime light.

Hydrogen being very sparingly soluble in water may be collected over this liquid; but if it is wanted dry, it must be collected over mercury.

It has been stated that hydrogen, disengaged by galvanism at a low temperature, is more active than that obtained by the ordinary processes, but this fact has not yet been sufficiently demonstrated.

## COMBINATIONS OF HYDROGEN WITH CHLORINE, BROMINE, IODINE, AND FLUORINE.

**Hydrochloric Acid** $\left.\begin{matrix}\mathrm{H}\\\mathrm{Cl}\end{matrix}\right\}$.—Hydrochloric acid is obtained by gently heating chloride of sodium with sulphuric acid.

$$\underset{\text{Chloride of sodium.}}{2\left(\left.\begin{matrix}\mathrm{Na}\\\mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}\mathrm{SO}^{2\prime\prime}\\\mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right)} = \underset{\text{Sulphate of sodium.}}{\left(\left.\begin{matrix}\mathrm{SO}^{2\prime\prime}\\\mathrm{Na}^2\end{matrix}\right\}\mathrm{O}^2\right)} + \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{Cl}\end{matrix}\right\}\right)}$$

It can also be obtained by leaving a mixture of equal volumes of chlorine and hydrogen for twenty-four hours in diffused light.

Hydrochloric acid is gaseous, but it can be liquefied under the influence of strong pressure; its density is equal to the mean of the densities of its components; it is colourless, and has a very irritating odour.

Hydrochloric acid is very soluble in water. This liquid dissolves about 500 times its volume. The solution constitutes a very acid liquid, giving off fumes when exposed to the air, and is obtained by means of Woulf's apparatus; when distilled, it loses part of its hydrochloric acid, but another part remains intimately combined with the liquid.

On account of its great solubility in water, hydrochloric acid gas should be collected over mercury.

The solution of hydrochloric acid can be exposed for any length of time to the air without decomposing. At a red heat, oxygen decomposes this acid by setting its chlorine free; but, in order to make this operation succeed, a great excess of oxygen in proportion to the chlorine must be employed. We have seen that, in the inverse conditions, chlorine decomposes water.

Hydrochloric acid does not act on mercury, but it dissolves potassium, sodium, iron, zinc, etc., with great facility, and then a chloride is formed and hydrogen is disengaged.

Iodine and bromine have no action upon this acid.

Bases and basic anhydrides react on it, giving rise to metallic chlorides and water.

$$\text{1st.}\quad \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}} + \underset{\text{Hydrate of potassium.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Chloride of potassium.}}{\left.\begin{matrix}K\\Cl\end{matrix}\right\}} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

$$\text{2nd.}\quad \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Anhydrous oxide of sodium.}}{\left(\left.\begin{matrix}Na\\Na\end{matrix}\right\}O\right)} = \underset{\text{Chloride of sodium.}}{2\left(\left.\begin{matrix}Na\\Cl\end{matrix}\right\}\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

Added to the solution of a salt of silver, hydrochloric acid produces a white precipitate of chloride of silver which is quite insoluble in water.

$$\underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}} + \underset{\text{Nitrate of silver.}}{\left(\left.\begin{matrix}NO^2\\Ag\end{matrix}\right\}O\right)} = \underset{\text{Nitric acid.}}{\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)} + \underset{\text{Chloride of silver.}}{\left.\begin{matrix}Ag\\Cl\end{matrix}\right\}}$$

The composition of hydrochloric acid can be determined analytically and synthetically.

ANALYTICALLY.—A known volume of this acid, in a gaseous state and perfectly dry, is introduced into a curved tube placed over a cup of mercury (fig. 17): in the curved part of this tube is placed a globule of sodium, and heat is gently applied. The metal takes the chlorine and sets free pure hydrogen. This hydrogen only occupies half the volume which was occupied by the hydrochloric acid gas.

| | |
|---|---|
| If from the density of hydrochloric acid . . . | 1·2474 |
| we subtract half the density of hydrogen . . . | 0·0345 |
| there remains . . . . . . . . . . . | 1·2129 |

which is about half the density of chlorine.

A volume of hydrochloric acid gas contains therefore half a volume of chlorine and half a volume of hydrogen united without condensation.

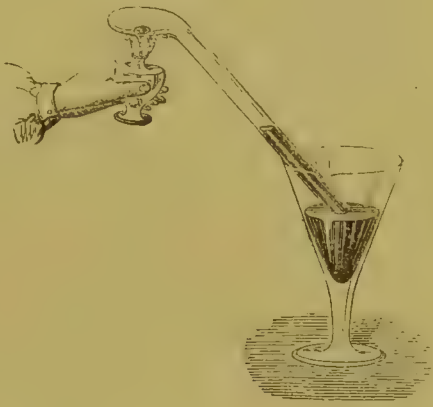


Fig. 17.

LEEDS SCHOOL O MEDICINE

Synthetically.—Two known volumes of hydrogen and chlorine are mixed, taking care that the hydrogen be in excess; they must be left for twenty-four hours in diffused light, and then the hydrochloric acid produced must be absorbed by potassium. The gas which remains is pure hydrogen, of which the volume must be determined, and this, subtracted from the volume of hydrogen which the mixture contained, gives the combined hydrogen. Then, as a volume of chlorine takes a volume of hydrogen to form hydrochloric acid, and as moreover no contraction is observed during the combination of these gases, the conclusion arrived at is, that a volume of chlorine, on uniting with a volume of hydrogen, gives two volumes of hydrochloric acid.

From this knowledge of the volumes which enter into combination, it is easy to arrive at their composition by weight; and if we consider that the weights of equal volumes of chlorine, hydrogen, and hydrochloric acid are proportional to the respective densities of these gases, we can place the proportions:

$$1{\cdot}2474 : 1{\cdot}2129 :: 100 : x; \text{ that is to say, } x = \frac{1{\cdot}2129 \times 100}{1{\cdot}2474} = 97{\cdot}24$$

and

$$1{\cdot}2474 : 0{\cdot}0345 :: 100 : x; \text{ that is to say, } x = \frac{0{\cdot}0345 \times 100}{1{\cdot}2474} = 2{\cdot}76$$

which gives for the centesimal composition of hydrochloric acid:

| | |
|---|---|
| Chlorine . . . . . . . . . . . | 97·24 |
| Hydrogen . . . . . . . . . . . | 2·76 |
| | 100·00 |

Hydrochloric acid diluted with water is sometimes employed in medicine to make rubefacient footbaths.

**Hydrobromic Acid.**—Pure hydrobromic acid cannot be obtained by making sulphuric acid act on a bromide, as sulphuric acid partially decomposes hydrobromic acid.

It is obtained by causing water to act on the bromide of phosphorus.

$$\underset{\text{Bromide of phosphorus.}}{\left(PBr^3\right)} + 3\underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Phosphorous acid.}}{\left(\left.\begin{matrix}P'''\\H^3\end{matrix}\right\}O^3\right)} + 3\underset{\text{Hydrobromic acid.}}{\left(\left.\begin{matrix}H\\Br\end{matrix}\right\}\right)}$$

The operation is usually conducted so that the bromide is produced and destroyed in the same process: the bromine is made to fall drop by drop into a vase which contains amorphous phosphorus and water.

Hydrobromic acid can also be obtained by the direct action of bromine on hydrogen; but in order that the combination may take place, a mixture of hydrogen and bromine vapour must be subjected to a red heat, and even then it is never complete.

The properties of hydrobromic acid are similar to those of hydrochloric acid; nevertheless, the two following differences exist:

1st. The solution of hydrobromic acid exposed to air becomes coloured by a little of the bromine being set free without the decomposition continuing. Nothing of the kind can be produced with hydrochloric acid.

2nd. Under the influence of chlorine, hydrobromic acid sets free bromine, and at the same time hydrochloric acid is formed.

**Hydriodic Acid.**—This acid is prepared by decomposing iodide of phosphorus by water. In order that the iodide of phosphorus may be produced and decomposed in the same operation, a mixture of iodine and phosphorus, with a small quantity of water, is heated in a retort.

Hydriodic acid can also be obtained in solution by the decomposition of hydrosulphuric acid under the influence of iodine.

$$2\underset{\text{Hydrosulphuric acid.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}S\right)} + 2\underset{\text{Iodine.}}{\left(\left.\begin{matrix}I\\I\end{matrix}\right\}\right)} = 4\underset{\text{Hydriodic acid.}}{\left(\left.\begin{matrix}H\\I\end{matrix}\right\}\right)} + \underset{\text{Sulphur.}}{\left.\begin{matrix}S\\S\end{matrix}\right\}}$$

It cannot be prepared by direct synthesis, as iodine and free hydrogen do not react on each other under any conditions.

The characters which distinguish hydriodic acid from the two preceding acids are the following:—

1st. The solution of hydriodic acid undergoes a continuous decomposition when brought into contact with air, and forms water and free iodine.

$$4\underset{\text{Hydriodic acid.}}{\left(\left.\begin{matrix}H\\I\end{matrix}\right\}\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} = 2\underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + 2\underset{\text{Iodine.}}{\left(\left.\begin{matrix}I\\I\end{matrix}\right\}\right)}$$

The metalloid is at first dissolved, colouring the liquid brown. As the quantity of hydriodic acid which the liquid contains diminishes constantly, while that of the free iodine increases, this latter body can at last no longer be held in solution, and is deposited in very voluminous crystals.

2nd. Hydriodic acid is decomposed by chlorine and by bromine, either of which set iodine free.

$$\underset{\text{Hydriodic acid.}}{2\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{I}\end{matrix}\right\}\right)} + \underset{\text{Bromine.}}{\left.\begin{matrix}\mathrm{Br}\\\mathrm{Br}\end{matrix}\right\}} = \underset{\text{Hydrobromic acid.}}{2\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{Br}\end{matrix}\right\}\right)} + \underset{\text{Iodine.}}{\left.\begin{matrix}\mathrm{I}\\\mathrm{I}\end{matrix}\right\}}$$

On the contrary, if hydriodic acid be made to act on bromide or chloride of silver, hydrobromic or hydrochloric acid would be produced, and iodide of silver.

$$\underset{\text{Chloride of silver.}}{\left.\begin{matrix}\mathrm{Ag}\\\mathrm{Cl}\end{matrix}\right\}} + \underset{\text{Hydriodic acid.}}{\left.\begin{matrix}\mathrm{H}\\\mathrm{I}\end{matrix}\right\}} = \underset{\text{Iodide of silver.}}{\left.\begin{matrix}\mathrm{Ag}\\\mathrm{I}\end{matrix}\right\}} + \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}\mathrm{H}\\\mathrm{Cl}\end{matrix}\right\}}$$

3rd. Hydriodic acid is decomposed by mercury, forming iodide of mercury and free hydrogen.

$$\underset{\text{Hydriodic acid.}}{2\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{I}\end{matrix}\right\}\right)} + \underset{\text{Mercury.}}{\mathrm{Hg}''} = \underset{\text{Biniodide of mercury.}}{\left(\left.\begin{matrix}\mathrm{Hg}''\\\mathrm{I}^2\end{matrix}\right\}\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}}$$

This property is the reason why hydriodic acid gas cannot be collected over mercury, and as its great solubility prevents its being collected over water, it is necessary to use the same process as for chlorine. Its great density causes it to displace air readily.

As hydriodic acid cannot be collected over mercury it cannot be analyzed; but if we subtract from its density the half of the density of hydrogen, a number remains evidently equal to the half of the density of the vapour of iodine; moreover, this acid obeys the same general system of reactions as hydrochloric and hydrobromic acids, and, like them, it is therefore formed of half a volume of hydrogen united, without condensation, to half a volume of the vapour of iodine.

**Hydrofluoric Acid.**—This compound is prepared by the action of sulphuric acid on the fluoride of calcium.

$$\underset{\text{Fluoride of calcium.}}{\left(\left.\begin{matrix}\mathrm{Ca}''\\\mathrm{Fl}^2\end{matrix}\right\}\right)} + \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}\mathrm{SO}^{2''}\\\mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right)} = \underset{\text{Sulphate of calcium.}}{\left(\left.\begin{matrix}\mathrm{SO}^{2''}\\\mathrm{Ca}''\end{matrix}\right\}\mathrm{O}^2\right)} + \underset{\text{Hydrofluoric acid.}}{2\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{Fl}\end{matrix}\right\}\right)}$$

The product thus prepared is liquid at the ordinary temperature, but when heated with phosphoric anhydride, the water which it contains is absorbed, and hydrofluoric acid is obtained in a gaseous state, like its two congeners. Hydrofluoric acid has much greater stability than hydrochloric acid. It acts on glass, which property can be utilized for engraving on this body; and by reacting on oxide of silver, hydrofluoric acid forms a soluble fluoride of silver.

Hydrofluoric acid is a powerful poison; if a few drops fall on the skin they produce a burn which is slow to heal, and is accompanied by inflammation.

These various properties distinguish hydrofluoric acid from the three preceding hydracids, to which by its other characters it is related.

This analogy enables us to give to this acid the formula $\left.\begin{matrix}H\\Fl\end{matrix}\right\}$; though isolated fluorine not being known, a certain analysis cannot be made, and the facility with which it acts on glass has prevented its vapour density being determined, and consequently, also, its molecular weight.

## GENERAL REMARKS ON THE MONATOMIC METALLOIDS.

There is little to be said concerning these bodies from a general point of view, that is to say, concerning any general theory of the combinations to which they can give rise. Each of them having a capacity for saturation equal to 1, can only combine with a single atom of another monatomic body; hence the number of their combinations is very limited.

Terchloride of iodine ($ICl^3$) seems an exception to this. M. Kékulé supposes that it is the result of the union of a molecule of chlorine $\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}$ with a molecule of protochloride of iodine $\left.\begin{matrix}I\\Cl\end{matrix}\right\}$. According to this hypothesis, the chlorine would be united to the protochloride as the water of crystallization is to the different substances which enter into the composition of hydrated crystals. The perchloride of iodine would then be written:

$$\left(\left.\begin{matrix}I\\Cl\end{matrix}\right\}\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}\right)$$

But the existence of the body $\left(I''' \left\{\begin{matrix}OC^2H^3O\\OC^2H^3O\\OC^2H^3O\end{matrix}\right.\right)$ which results from the replacement of three atoms of chlorine of this chloride, by three of oxacetyl, proves that iodine is really triatomic, though it nearly always acts as monovalent.

## SECOND GROUP (BIATOMIC METALLOIDS).

### OXYGEN $\left.\begin{matrix}O\\O\end{matrix}\right\}$

**Atomic Weight = 16. Molecular weight = 32.**

Oxygen can be prepared in several different ways:

1st. By heating mercuric oxide, which is resolved into oxygen and mercury.

$$\underset{\text{Mercuric oxide.}}{2(HgO)} = \underset{\text{Mercury.}}{2Hg} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}}$$

The flame of a spirit lamp suffices for this operation (fig. 18).

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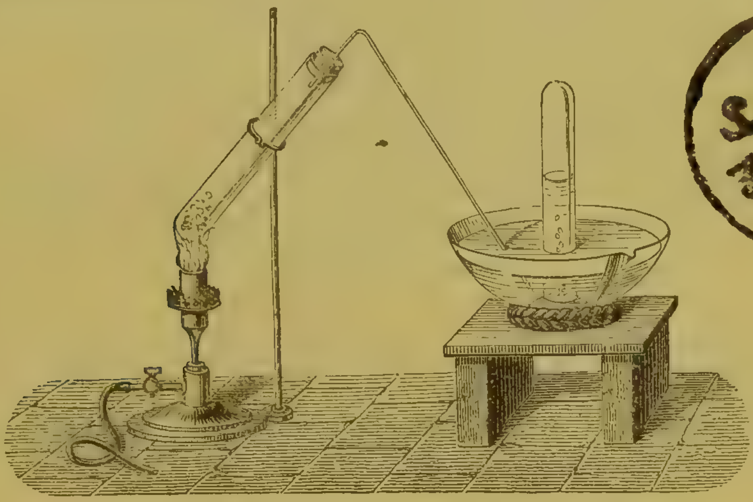


Fig. 18.

2nd. By heating the binoxide of manganese to redness in an earthenware retort, when it gives off the third part of its oxygen.

$$\underset{\text{Peroxide of manganese.}}{3(MnO^2)} = \underset{\text{Red oxide of manganese.}}{(Mn^3O^4)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}}$$

As binoxide of manganese always contains a little carbonate of the same metal, the oxygen thus produced is accompanied by carbonic anhydride. To remove this, before collecting the gas, it is made to pass through a phial with three tubes arranged like Woulf's apparatus, and containing a solution of potash (fig. 19).

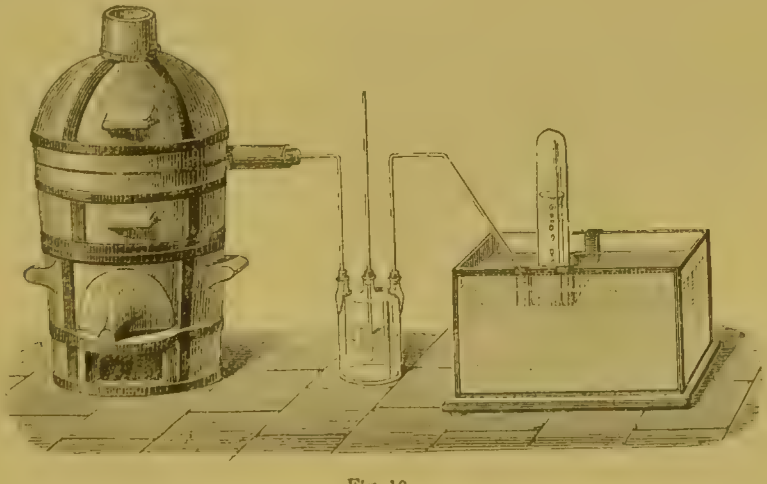


Fig. 19.

3rd. By gently heating binoxide of manganese with sulphuric acid, when sulphate of manganese and water are formed, and half the oxygen which the binoxide contained, is disengaged (fig. 20).

$$\underset{\text{Binoxide of manganese.}}{2\left(\mathrm{MnO}^2\right)} + \underset{\text{Sulphuric acid.}}{2\left(\left.\begin{matrix}\mathrm{SO}^{2''}\\ \mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right)} =$$

$$\underset{\text{Sulphate of manganese.}}{2\left(\left.\begin{matrix}\mathrm{SO}^2\\ \mathrm{Mn}''\end{matrix}\right\}\mathrm{O}^2\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\}}$$

As carbonate of manganese when cold loses by the action of sulphuric acid all the carbonic anhydride which it is capable of disengaging, it suffices to leave the preceding mixture to itself for some time before heating it, in order that the oxygen collected may be nearly pure.

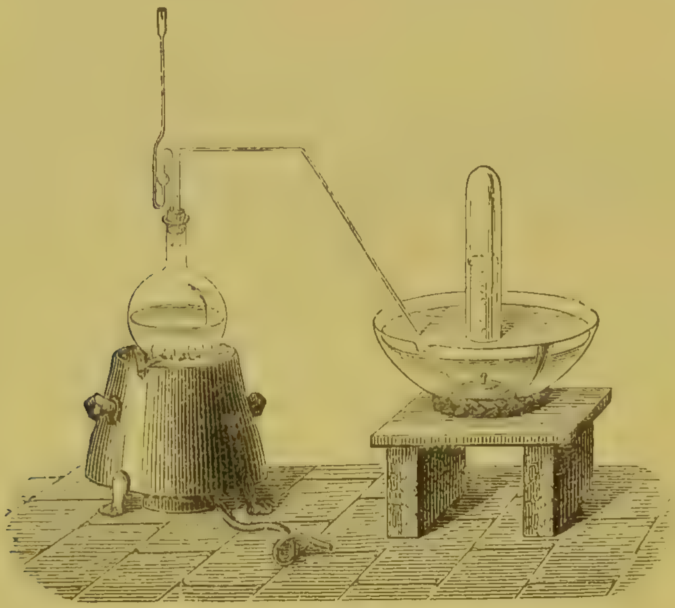


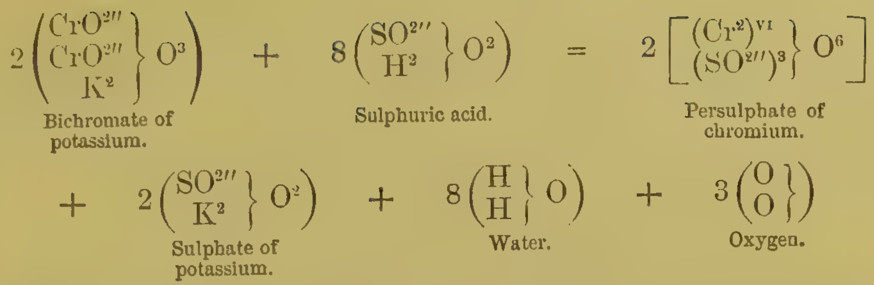
Fig. 20.

4th. By heating chlorate of potassium; oxygen is disengaged, and there remains chloride of potassium.

$$\underset{\text{Chlorate of potassium.}}{2\left(\left.\begin{matrix}\mathrm{ClO}^2\\ \mathrm{K}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\text{Chloride of potassium.}}{2\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\text{Oxygen.}}{3\left(\left.\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\}\right)}$$

This reaction is greatly assisted by mixing with the chlorate of potassium a small quantity of oxide of copper, sesquioxide of iron, or binoxide of manganese. These oxides act by catalysis without taking part in the reaction.

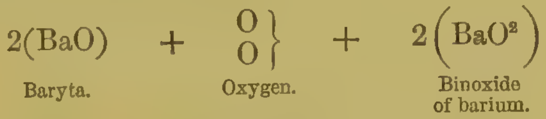
5th. By gently heating bichromate of potassium with sulphuric acid; oxygen is formed, and at the same time water, persulphate of chromium, and sulphate of potassium.



$$2\underset{\text{Bichromate of potassium.}}{\left(\left.\begin{matrix}CrO^{2''}\\CrO^{2''}\\K^2\end{matrix}\right\}O^3\right)} + 8\underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)} = 2\underset{\text{Persulphate of chromium.}}{\left[\left.\begin{matrix}(Cr^2)^{vi}\\(SO^{2''})^3\end{matrix}\right\}O^6\right]}$$

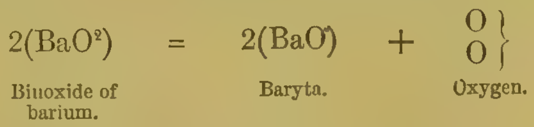
$$+ 2\underset{\text{Sulphate of potassium.}}{\left(\left.\begin{matrix}SO^{2''}\\K^2\end{matrix}\right\}O^2\right)} + 8\underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + 3\underset{\text{Oxygen.}}{\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\right)}$$

6th. When baryta is heated to a low red heat in a current of dry air, it absorbs oxygen, and is transformed into binoxide of barium.



$$\underset{\text{Baryta.}}{2(BaO)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} + \underset{\text{Binoxide of barium.}}{2\left(BaO^2\right)}$$

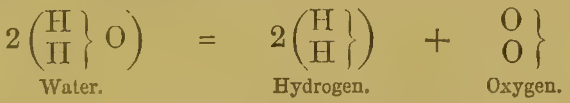
If the current of air be then arrested, and the temperature increased to a strong red heat, the binoxide of barium is destroyed with the production of oxygen and the reproduction of baryta.



$$\underset{\text{Binoxide of barium.}}{2(BaO^2)} = \underset{\text{Baryta.}}{2(BaO)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}}$$

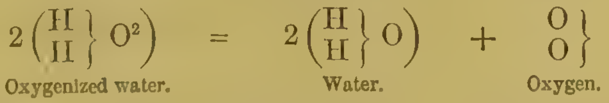
With the same baryta a great quantity of oxygen can be taken from the air. This oxide, nevertheless, cannot be used indefinitely; at the end of a certain time it loses its power of absorbing the oxygen of the air on account of a species of vitrification which is produced on its surface.

7th. By the decomposition of water by the galvanic battery: care must be taken to acidulate the liquid with a little sulphuric acid, in order to make it a better conductor of electricity. The electrodes ought to be of platinum, or they will oxydize instead of the oxygen being disengaged. The oxygen is collected at the positive pole.



$$2\underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = 2\underset{\text{Hydrogen.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}}$$

8th. Oxygen can be obtained by decomposing oxygenized water by certain bodies which exercise on it a catalytic action; pulverulent silver, for instance; oxygen is disengaged and water remains.



$$2\underset{\text{Oxygenized water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O^2\right)} = 2\underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}}$$

When we wish to make nascent oxygen act on other substances, we prefer the mode of preparation by the action of sulphuric acid on bichromate of potassium or binoxide of manganese. When, on the contrary, we wish to collect free oxygen, we prefer to obtain it from chlorate of potassium.

Oxygen is gaseous at all the temperatures and under all the pressures

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which we can produce. Its density is 1·105; water dissolves 0·046 of its volume; it is tasteless, inodorous, and colourless. Oxygen is the principal body which maintains the combustion of organic substances. If a match or a taper in a state of incandescence be plunged into it, these bodies will burst into flame and burn very brightly.

Sulphur and phosphorus burn in oxygen with extraordinary brilliance. This is also the case with iron: a spiral lamina of this metal, to which is attached a piece of lighted tinder, takes fire when placed in pure oxygen. The heat disengaged is such that the oxide of iron produced encrusts the glass in which the experiment takes place, even after it has passed through some centimetres of water.

We have already seen that oxygen combines with hydrogen with explosion, either when the mixture of the two gases is ignited, or when it is placed in contact with spongy platinum.

Oxygen has a great affinity for carbon: among metals, cæsium, rubidium, potassium, sodium, and lithium, are those with which it combines with the greatest energy.

Oxygen is the only gas which can support respiration; if it were pure, this function would be too active, and inflammation of the respiratory organs would result. This gas enters into the composition of atmospheric air, of which it forms about the fifth part.

Allotropic States.—Disengaged by means of the galvanic battery at a low temperature, oxygen possesses much greater activity than when obtained by any other process. It can then combine directly with silver and mercury, set free iodine from iodide of potassium, burn organic substances when cold, etc.; and, further, it possesses a peculiar electrical odour. Oxygen thus modified is called ozone.

Mr. Andrews believed that ozone contained eight atoms of oxygen, but fresh experiments have induced him to abandon that opinion.

When oxygen is transformed into ozone, a contraction is observed in the mass; but when the ozone which the gas contains is absorbed, no contraction is produced.*

Two theories may account for this phenomenon: the first consists in admitting that the ozone is in such a state of condensation that its disappearance by the side of a great excess of oxygen gives no appreciable diminution of volume.

By the second, we suppose a molecule of ordinary oxygen $\left.\begin{matrix}O\\O\end{matrix}\right\}$ to be united in the ozone to an atom of allotropic oxygen $\ominus$ with contraction of a third; the ozone will then answer to the formula $\left.\begin{matrix}O\\O\end{matrix}\right\}\ominus$, and will contain a volume of ordinary oxygen equal to its own. If we cause reaction to take place between ozone and a body which is oxydized by it, there remains ordinary oxygen, which occupies exactly the volume which the ozone occupied; there is no contraction.

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* M. Soret has recently absorbed the whole molecule of ozone by means of oil of turpentine.—Trans.

This is the most probable theory; it represents ozone by the formula $\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\ominus\right)$, which makes the $H^2$ of oxygenized water to be replaced by O.

At 300° ozone is converted into ordinary oxygen. To detect the presence of ozone, a piece of paper steeped in a solution of iodide of potassium containing starch is used; the iodine set free coming in contact with the starch, the paper assumes a blue tint.

As other bodies give the same reaction it is preferable to use reddened litmus paper steeped in a solution of iodide of potassium; ozone decomposes this salt, and forms oxide of potassium: this, on contact with moisture, makes the litmus blue. Care must be taken to place by the side of the ozonoscopic paper another paper of reddened litmus, to prove that the blue colour is really due to ozone, and not to the accidental presence of a small quantity of ammonia.

Ozone exists in woods and fields, and wherever there is active vegetation. In large towns, on the contrary, and in houses, or wherever there are numbers of men or animals collected, ozone disappears, or at least diminishes.

It is also stated that ozone disappears during great epidemics. Are these epidemics owing to the disappearance of the ozone, which, being no longer in sufficient quantity to destroy the miasmata, enable these to accumulate? or are they not rather owing to the production of such a quantity of miasmata that the ozone is not sufficient to destroy them? In other words, are epidemics the cause or the result of the disappearance of ozone? At present this is undetermined.

M. Schœnbein, to whom we owe the discovery of ozone, admits another allotropic state of oxygen, which he calls antozone. Ozone would be oxygen negatively electrified, which would form $\ominus$, and antozone oxygen positively electrified $\oplus$. These two oxygens would have the property of reciprocally destroying each other, and thereby passing again to the state of ordinary oxygen by means of the reciprocal neutralization of their electricities; both would be called in a general way active oxygen, in order to indicate their chemical energy. M. Schœnbein has stated that when binoxide of barium is made to act on a mixture of sulphuric acid and permanganate of potassium in the cold, active oxygen is obtained differing somewhat from ozone; and further, it appears that this gas mixed with ozone brings the latter back to the state of ordinary oxygen, itself also returning to the same state.

This would lead us to consider this allotropic state of oxygen as being antozone. According to the hypothesis we have admitted as to the constitution of ozone, the formula of antozone would be $\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\oplus\right)$. Quite recently M. Baudrimont has announced new experiments which would justify M. Schœnbein's theory, but as he has not published them we cannot pronounce on their value.

### Combinations of Oxygen with Hydrogen.

**Water** $\left(H^2O\right) = \left(\left.\begin{matrix}H\\H\end{matrix}\right\} O\right)$.—Until the end of the last century water was considered to be a simple body. Cavendish was the first to observe that this substance is formed by the combustion of hydrogen, and from this fact he deduced hypothetically the composition of water. Lavoisier soon verified this conjecture. He caused the vapour of water to pass through a porcelain tube heated to redness and containing iron filings, and found that decomposition took place; that oxygen remained fixed by the iron, the weight of which was increased, while hydrogen was disengaged. It was not until later that the quantitative composition of water was exactly determined.

This determination may be made either analytically or synthetically.

Analytically.—Water is placed in a glass vessel A (fig. 21), the bottom of which is pierced by two holes. Through these holes two platinum wires are fixed, whose ends terminate in graduated test tubes B and C, full of water, and inverted in the vessel. Then the wires D and E are placed in communication with the opposite poles of a galvanic battery. Immediately gas bubbles are formed at the ends of the wires and are collected in the tubes. If after a certain time the volume of gas produced be measured, it will be found that the gas developed at the positive pole occupies half the volume of that which is developed at the negative pole; and further, that the first of these gases is pure oxygen and the second pure hydrogen. To facilitate this experiment, the water of the voltameter (the name of the apparatus we have just described) should be acidulated with a little sulphuric acid to make it a better conductor.

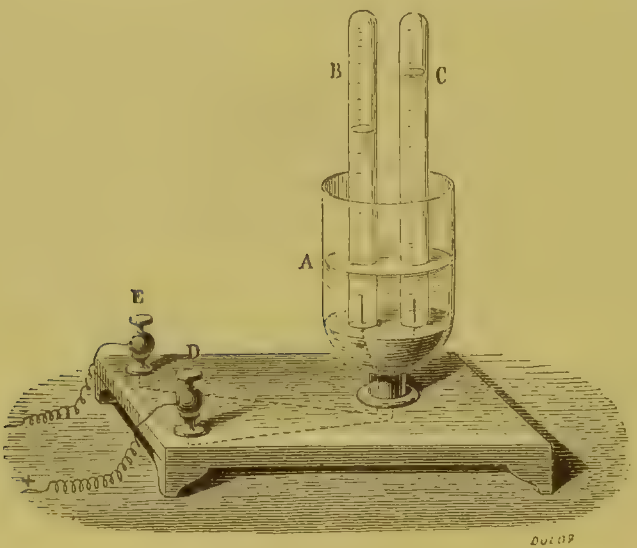

Fig. 21.

Water therefore is formed of two volumes of hydrogen and one of oxygen. Adding to

| | |
|---|---|
| the double density of hydrogen . . . . . . | 0·1384 |
| the density of oxygen . . . . . . . . . . | 1·105 |
| we obtain the number . . . . . . . . . . | 1·2434 |

which represents very nearly the double of the density of the vapour of water, 0·622; we thence conclude that the two volumes of hydrogen and the volume of oxygen are condensed into two volumes.

Knowing the density of hydrogen, of oxygen, and of the vapour of water, it is easy to transform the preceding numbers into weights.

SYNTHETICALLY.—We can operate either by the aid of the eudiometer or by M. Dumas' process.

*By the Eudiometer.*—This is a thick bell-glass (fig. 22) with two holes in its upper part, in which are fastened two iron rods, terminated at each end by a little ball. The two internal balls C and D nearly touch, while of those on the exterior, one B is free, and the other A has attached to it a metallic chain AF, which is longer than the eudiometer. At the lower part of the bell-glass is an iron bar, on which can be adjusted at will a moveable slide of the same metal E, having a narrow hole in the centre.

In determining the composition of water by this instrument, we introduce into it a measured volume of hydrogen; let this be $4^{cc}$, and a volume of oxygen also measured, which we will suppose equal to $4^{cc}$. This done, and the eudiometer being closed at its lower end by the metallic piece of which we have spoken, and being placed in a bath of mercury, the chain AF is placed in the mercury, and a charged electrophorus is brought to the ball B. A spark passes between the electrophorus and this ball, and another between the two interior balls D and C. This latter spark causes the combination of the oxygen and hydrogen.

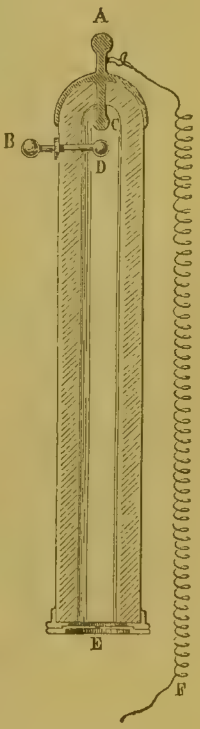

Fig. 22.

After the explosion, the gas remaining is poured into a graduated tube and measured. In the conditions we have supposed, there would remain $2^{cc}$ of pure oxygen; the oxygen that has disappeared would therefore occupy $2^{cc}$, and the hydrogen $4^{cc}$; consequently, the water formed is composed of two volumes of oxygen and four volumes of hydrogen, or, reducing the proportion to the most simple expression, of two volumes of hydrogen and one volume of oxygen.

*M. Dumas' Process.*—M. Dumas has invented a process in which weights are employed instead of volumetric measures. His apparatus consists of three parts: the first of which is intended for the production and purification of the hydrogen ; the second for the synthesis of the water, and the third for the collection of the water formed in the second.

The hydrogen is produced in the ordinary manner in a flask with two tubulures (fig. 23) A, by means of sulphuric acid and zinc. It is made to traverse : 1st, two U-shaped tubes *bb*, containing sulphate of silver ; this salt absorbs the phosphoric and arsenical compounds which the hydrogen contains, and which are due to the impurities of the zinc : 2nd, a tube *c*, containing acetate of lead ; this body absorbs the last traces of the sulphuretted hydrogen coming from the same source : 3rd, two tubes *dd* full of potash ; this base absorbs an oil which also arises from the impurities of the zinc as well as traces of acetic acid vapour resulting from the action of sulphuretted hydrogen on the acetate of lead in the tube C : 4th, two U-shaped tubes *ee* full of phosphoric anhydride to dry the gases : 5th, a small tube full of pumice-stone steeped in sulphuric acid, which is weighed both before and after the operation ; this tube ought always to maintain the same weight, and so indicate that nothing has deposited in its interior, and consequently that the gas is dry.

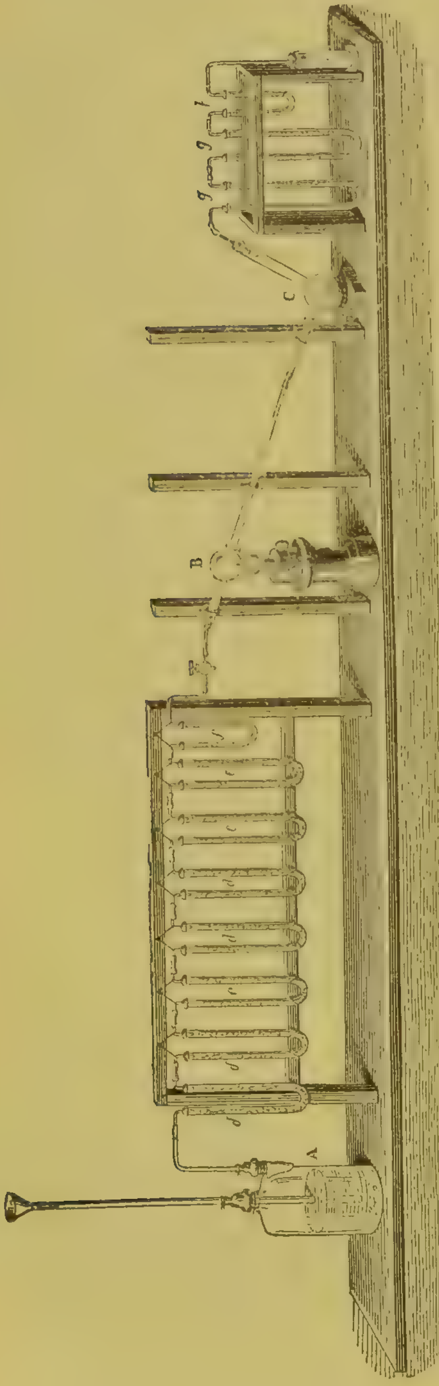

Fig. 23.

Pure hydrogen then passes into the second part of the apparatus, constituted of a glass globe with two tubes B, in which very dry oxide of copper has been placed.

The gas on coming out of this globe passes into the third part of the apparatus. This third part is composed thus : $\alpha$ of a globe with two tubes C ; $\beta$ of two U-tubes *gg* full of pumice-stone moistened with sulphuric acid ; $\gamma$, of a small test tube analogous to the two preceding ones.

When this apparatus is used the globe B is weighed after having had oxide of copper introduced into it, let $P$ be its weight; the globe C is also weighed, and likewise the two tubes with acidulated pumice $gg$, let $p'$ be the sum of their weights; then the apparatus is mounted, and hydrogen is passed into it until all the air is entirely expelled, after which the globe containing the oxide of copper is heated, continuing the gaseous current. Under the simultaneous influences of heat and hydrogen, the oxide of copper loses its oxygen and water is formed. This water in vapour passes into the globe C, where it becomes partly condensed, then into the tubes $gg$, which retain all that which was not already condensed.

When the operation has lasted long enough, the current of hydrogen is arrested, and it is replaced by a current of air, after the globe B has become cold; thus the apparatus is again filled with air, which is necessary in order to avoid an error in weight which would result from the difference in the density of hydrogen and air.

The apparatus being taken to pieces, the globe B is weighed on the one hand, and on the other the globe C with the tubes $gg$.

The weight $p$ of the globe B is less than its weight $P$ before the experiment, on account of the loss of oxygen which the oxide of copper has experienced. $P-p$ represents the weight of this oxygen. The globe C and the tubes $gg$ have together a weight $P'$ greater than their weight $p'$ before the experiment, on account of the water which is fixed therein. $P'-p'$ represents the weight of the water formed.

Finally, on subtracting from the water $P'-p'$ the weight of the oxygen $P-p$, the difference gives the weight of the hydrogen which this water contains.

On transforming the composition found into hundred parts, by means of proportion, we see that 100 parts of water contain: hydrogen, 11·11; oxygen, 88·89.

Water is liquid at ordinary temperatures, at 0° it becomes solid, and at 100° it vaporizes. If water be carefully protected from agitation, it can be cooled to $-12°$ without becoming congealed, but the least agitation induces the immediate congelation of the mass, and the temperature rises to 0°.

Ice is crystallized; but its crystals are so intermingled that they appear under the form of a continuous transparent mass. It is as snow that we can best study their form, which is that of prisms belonging to the fourth system, grouped in stars.

Liquid water presents a maximum density at 4°, and it is at this temperature that its density is considered as equal to 1. The density of ice is 0·94, and the density of the vapour of water 0·6234.

Pure water has neither smell nor taste; it has very great solvent powers, but these do not extend to fatty substances, nor in general to organic substances very much hydrogenized or highly carbonized.

Water combines directly with acid anhydrides to form acids, and with basic anhydrides to form bases, when the acids or bases which would arise have an even atomicity; when, on the contrary, their atomicity is uneven, they are still produced, but by double decomposition and not by direct combination.

$$\underset{\text{Sulphuric anhydride.}}{(SO^3)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)}$$

$$\underset{\text{Anhydrous oxide of potassium.}}{\left(\left.\begin{matrix}K\\K\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Hydrate of potassium.}}{2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)}$$

The water of lakes, rivers, and seas, is not pure. The surest means of purifying it is by distillation. This is performed in apparatus called alembics or stills; these apparatus are composed of three parts: one in which the water is reduced into vapour; another, where the condensed vapour is received, and the third which serves as a communication between the other two. This third part usually consists of a long spiral tube.

In cold countries, instead of distillation, congelation may be used. When only a part of the mass of impure water is congealed, the impurities accumulate in the portion of water that remains liquid, and the ice is almost pure.

As an article of food, water ought to be aërated, and should only contain a very small quantity of salts in solution, and no appreciable quantity of organic matter. When it contains an excessive proportion of calcareous salts it produces indigestion; and when it contains organic substances it possesses septic properties which render its use dangerous.

Natural waters sometimes contain substances in solution sufficient to render them useful in medicine, and are then called mineral waters.

**Oxygenated Water, or Binoxide of Hydrogen** $\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O^2\right)$.—Oxygenated water is obtained by the reaction of hydrochloric acid on binoxide of barium.

$$\underset{\text{Binoxide of barium.}}{\left(Ba''O^2\right)} + \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\text{Oxygenated Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O^2\right)} + \underset{\text{Chloride of barium.}}{\left(\left.\begin{matrix}Ba''\\Cl^2\end{matrix}\right\}\right)}$$

Oxygenated water is very instable; under the influence of heat it is decomposed into water and oxygen; moreover, it gives rise to three curious orders of reactions.

Certain bodies decompose it into oxygen and water by catalytic action without themselves taking part in the reaction; as pulverulent metallic silver or platinum, etc.

Other bodies decompose oxygenated water, but then become oxidized themselves; such as oxide of zinc, oxide of strontium, etc.; and, finally, a third class of bodies, at the head of which oxide of silver must be placed, have the property of losing their oxygen under the influence of oxygenated water while it is also at the same time reduced.

$$\underset{\text{Oxygenated water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O^2\right)} + \underset{\text{Oxide of silver.}}{\left(\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}O\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Silver.}}{\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}}$$

This last reaction may be explained by supposing that the atoms of oxygen which leave the silver and water have more affinity for each other than for the bodies to which they were united, and that consequently they separate from these latter and unite together to form a molecule of free oxygen. M. Schœnbein even says that these atoms of oxygen are electrified, but each in a contrary manner. If it be so, we must conceive an oxygenated water electrified inversely to that known already. In fact, M. Baudrimont says he has obtained such a body by decomposing binoxide of manganese by processes he has not published.

### Combinations of Oxygen with Chlorine.

There exist several oxygenated compounds of chlorine. They are hypochlorous anhydride ($Cl^2O$), chlorous anhydride ($Cl^2O^3$), peroxide of chlorine ($ClO^2$), chloric acid ($ClHO^3$), and perchloric acid ($ClHO^4$).

Besides these, there seems to be an oxide of chlorine ($ClO$) in existence which is not accurately known.

**Hypochlorous Anhydride** ($Cl^2O$) is prepared by passing a current of chlorine in a perfectly dry state through a glass tube filled with oxide of mercury obtained by precipitating a per-salt of mercury by potash (fig. 24). The hypochlorous anhydride which disengages during this reaction is collected in a receiver placed in a freezing mixture.

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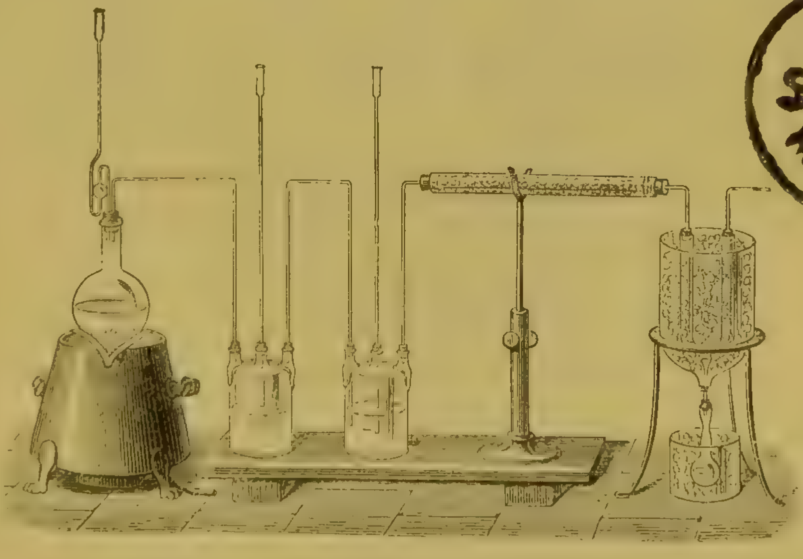


Fig. 24.

where the gas liquefies. Care must be taken during the operation to cool the tube which contains the oxide of mercury.

The following equation explains this reaction:

$$\underset{\text{Protoxide of mercury.}}{2\left(Hg''O\right)} + \underset{\text{Chlorine.}}{2\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}\right)} = \underset{\text{Oxychloride of mercury.}}{\left(Hg''^2OCl^2\right)} + \underset{\text{Hypochlorous anhydride.}}{\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}O\right)}$$

Hypochlorous anhydride is a deep red liquid, which boils at 20°; its vapour density is 2·997. Its odour resembles that of chlorine and iodine; water dissolves about 200 times its volume. In this case no double decomposition takes place between the water and the hypochlorous anhydride. If it did—if hypochlorous acid (ClHO) were to form—the proportion of gas dissolved ought to be much greater. The equation

$$\underset{\text{Hypochlorous anhydride.}}{(Cl^2O)} + \underset{\text{Water.}}{(H^2O)} = \underset{\text{Hypochlorous acid.}}{2(ClHO)}$$

would require that a kilogramme of water should dissolve 4833 grammes of hypochlorous gas, while the quantity dissolved is only 779 grammes.

The solution of hypochlorous anhydride has very strong oxidizing and bleaching properties. Gay-Lussac has observed that half a litre of this anhydride decolorizes as much indigo as a litre of pure chlorine. As half a litre of hypochlorous anhydride contains half a litre of chlorine and a quarter of litre of oxygen, and as moreover there is no reason why the chlorine, set free by the decomposition of the hypochlorous anhydride, should bleach more than if it had not been engaged in this combination, it must be concluded that a quarter of a litre of nascent oxygen decolorizes as much as half a litre of chlorine, or, in other words, that the bleaching power of nascent oxygen is double that of chlorine.

Hypochlorous anhydride is easily decomposed by hydrochloric acid; in this case water and free chlorine are formed.

$$\underset{\text{Hypochlorous anhydride.}}{\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}O\right)} + \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}Cl\\H\end{matrix}\right\}\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Chlorine.}}{2\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}\right)}$$

When gaseous, it explodes readily on a slight elevation of temperature.

When the hypochlorous anhydride is not required dry, it may very easily be obtained in solution by placing a diluted solution of oxide of mercury into a large bottle full of chlorine and shaking briskly.

The solution of hypochlorous anhydride often acts on contact with organic substances as if it contained hypochlorous acid, though in reality it does not. It is probable that in this case the organic substance causes the reaction of the hypochlorous anhydride and the water. Thus with ethylene the reaction is expressed by the following equation:—

$$\underset{\text{Hypochlorous acid.}}{\left(\left.\begin{matrix}Cl\\H\end{matrix}\right\}O\right)} + \underset{\text{Ethylene.}}{\left(C^2H^{4''}\right)} = \underset{\text{Chlorhydrin of glycol.}}{\left(C^2H^{4''}\left\{\begin{matrix}Cl\\OH\end{matrix}\right.\right)}$$

**Chlorous Anhydride** $Cl^2O^3$.—To prepare this, a mixture is made of three parts of arsenious anhydride and four parts of chlorate of potassium. This is pulverized and mixed with sufficient water to make a liquid paste, and 12 parts of nitric acid diluted with four parts of water are added. A small flask is filled up to the neck with the mixture, a disengagement tube is adapted, and the flask is gently heated in a water-bath after being covered with a cloth to avoid accident in case of explosion.

Under these conditions a greenish yellow gas is disengaged—a powerful decolorizer; its density is 2·646, and it bears a temperature of −20° without being liquefied.

Chlorous gas is soluble in water, and gives a beautiful yellow liquid. On combining with bases, it gives chlorites:

$$\underset{\text{Chlorous anhydride.}}{\left(Cl^2O^3\right)} + 2\underset{\text{Hydrate of potassium.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + 2\underset{\text{Chlorite of potassium.}}{\left(\left.\begin{matrix}ClO\\K\end{matrix}\right\}O\right)}$$

Chlorous anhydride detonates on a very slight elevation of temperature; it is also decomposed with explosion by several metalloids, such as sulphur, selenium, tellurium, iodine, phosphorus, arsenic, etc., which are oxidized at its expense.

Mercury also decomposes it; other metals are without action upon it.

In the preparation of this body, first, nitric acid reacts on chlorate of potassium, and gives chloric acid and potassic nitrate. Then chloric acid reacts on the arsenious anhydride which it causes to pass to the state of arsenic acid, while it itself becomes chlorous anhydride.

$$\text{1st.}\quad \underset{\text{Chlorate of potassium.}}{\left(\left.\begin{matrix}ClO^2\\K\end{matrix}\right\}O\right)} + \underset{\text{Nitric acid.}}{\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)} = \underset{\text{Nitrate of potassium.}}{\left(\left.\begin{matrix}NO^2\\K\end{matrix}\right\}O\right)} + \underset{\text{Chloric acid.}}{\left(\left.\begin{matrix}ClO^2\\H\end{matrix}\right\}O\right)}$$

$$\text{2nd.}\quad 2\underset{\text{Chloric acid.}}{\left(\left.\begin{matrix}ClO^2\\H\end{matrix}\right\}O\right)} + \underset{\text{Arsenious anhydride.}}{\left(\left.\begin{matrix}As'''\\As'''\end{matrix}\right\}O^3\right)} + 2\underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} =$$

$$2\underset{\text{Arsenic acid.}}{\left(\left.\begin{matrix}AsO'''\\H^3\end{matrix}\right\}O^3\right)} + \underset{\text{Chlorous anhydride.}}{\left(\left.\begin{matrix}ClO\\ClO\end{matrix}\right\}O\right)}$$

**Peroxide of Chlorine (Hypochloric Acid)** $ClO^2$.—This is obtained by carefully heating in a small tube by a water-bath (fig. 25) a mixture of sulphuric acid and chlorate of potassium broken into coarse fragments. The gas which forms is passed by a disengagement tube into a very cold receiver. Care must be taken that the water in the bath does not come up to the level of the mixture in the tube. It is also prudent to keep it cool while mixing.

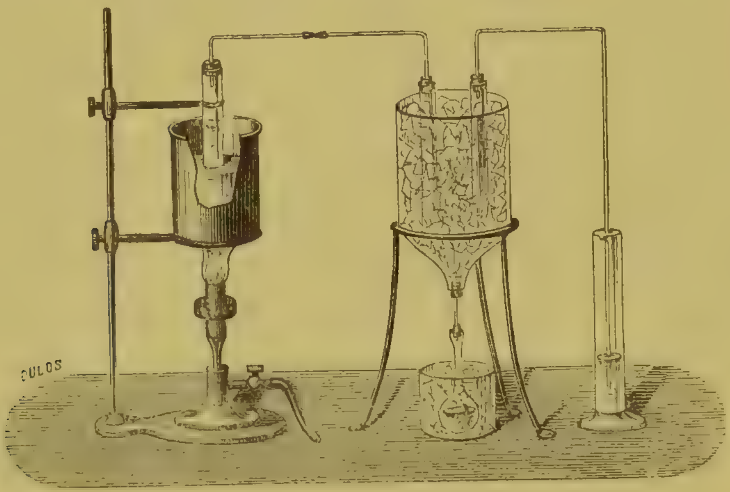


Fig. 25.

The reaction is expressed by the following equation:

$$\underset{\text{Chlorate of potassium.}}{3\left(\left.\begin{matrix}\mathrm{ClO^2}\\ \mathrm{K}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}\mathrm{SO^{2''}}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{O^2}\right)} =$$

$$\underset{\text{Water.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Perchlorate of potassium.}}{\left(\left.\begin{matrix}\mathrm{ClO^3}\\ \mathrm{K}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Peroxide of chlorine.}}{2\left(\mathrm{ClO^2}\right)} + \underset{\text{Sulphate of potassium.}}{\left(\left.\begin{matrix}\mathrm{SO^{2''}}\\ \mathrm{K^2}\end{matrix}\right\}\mathrm{O^2}\right)}$$

Peroxide of chlorine is gaseous at ordinary temperatures; it liquefies at —20°, forming a red liquid; its density in the gaseous state is 2·315; it is a very explosive body, soluble in water, and easily decomposed by mercury; bases transform it into a mixture of chlorate and chlorite.

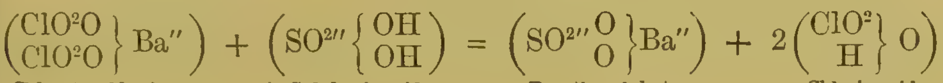
$$\underset{\text{Peroxide of chlorine.}}{2\left(\mathrm{ClO^2}\right)} + \underset{\text{Hydrate of potassium.}}{2\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\text{Potassic chlorite.}}{\left(\left.\begin{matrix}\mathrm{ClO}\\ \mathrm{K}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Potassic chlorate.}}{\left(\left.\begin{matrix}\mathrm{ClO^2}\\ \mathrm{K}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}$$

This reaction establishes an analogy between the peroxide of chlorine and hyponitric acid ($NO^2$), which is also converted into a mixture of nitrate and nitrite under the influence of bases (*see* Nitrogen); in consequence, it may be called *hypochloric acid.*

**Chloric Acid** ($ClHO^3$.)—In order to prepare this acid, whose anhydride is not stable, a concentrated solution of chlorate of potassium is treated with hydrofluosilicic acid. A double decomposition takes place; chloric acid is set free, and the potassium is precipitated in the state of hydrofluosilicate. Unfortunately, this precipitate is scarcely visible, so that an excess of hydrofluosilicic acid must be used, because the precise moment at which the precipitation is complete cannot be ascertained.

The liquor, therefore, contains a mixture of chloric and hydrofluosilicic acids; it is filtered, and hydrate of barium is added, which transforms the two acids into barytic salts. The hydrofluosilicate of barium thus formed, being insoluble, is precipitated, and the barytic chlorate remains in solution. It is filtered, and the chlorate of barium is decomposed by sulphuric acid. This acid ought to be added drop by drop, until a last drop produces no more precipitate. It is then filtered through asbestos, and the liquid is concentrated at the ordinary temperature by means of the air-pump.

The following equation shows the action of the sulphuric acid on the chlorate of barium:



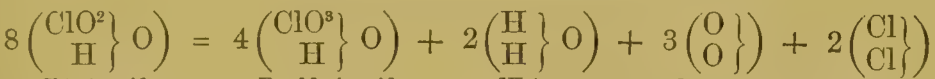
$$\underset{\text{Chlorate of barium.}}{\left(\left.\begin{matrix}\mathrm{ClO^2O}\\ \mathrm{ClO^2O}\end{matrix}\right\}\mathrm{Ba''}\right)} + \underset{\text{Sulphuric acid.}}{\left(\mathrm{SO^{2''}}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}\right.\right)} = \underset{\text{Barytic sulphate.}}{\left(\mathrm{SO^{2''}}\left.\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\}\mathrm{Ba''}\right)} + 2\underset{\text{Chloric acid.}}{\left(\left.\begin{matrix}\mathrm{ClO^2}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}$$

Chloric acid is a syrupy liquid of a yellow colour on account of the chlorine which it always contains in solution, and which arises from its partial decomposition. At 40° it decomposes into perchloric acid and chlorous anhydride; at the boiling point the decomposition is more complete, perchloric acid being formed, and chlorine and oxygen disengaged.

### *First Method of Decomposition.*

$$4\underset{\text{Chloric acid.}}{\left(\left.\begin{matrix}\mathrm{ClO^2}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\text{Chlorous anhydride.}}{\left(\left.\begin{matrix}\mathrm{ClO}\\ \mathrm{ClO}\end{matrix}\right\}\mathrm{O}\right)} + 2\underset{\text{Perchloric acid.}}{\left(\left.\begin{matrix}\mathrm{ClO^3}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}$$

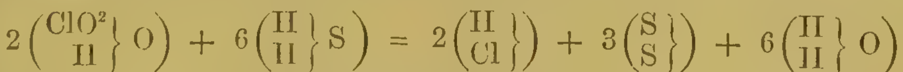
### *Second Method of Decomposition.*



$$8\underset{\text{Chloric acid.}}{\left(\left.\begin{matrix}\mathrm{ClO^2}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} = 4\underset{\text{Perchloric acid.}}{\left(\left.\begin{matrix}\mathrm{ClO^3}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + 2\underset{\text{Water.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + 3\underset{\text{Oxygen.}}{\left(\left.\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\}\right)} + 2\underset{\text{Chlorine.}}{\left(\left.\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right\}\right)}$$

Chloric acid, when brought into contact with tincture of litmus, at first colours it red like acids, but soon bleaches by oxidizing it.

It is a very instable body, and is in consequence a strong oxidant. Its instability is such that, if a drop be gently heated on a piece of paper, the paper takes fire and burns. Alcohol takes fire on contact with this acid. Hydro-sulphuric acid reduces it to the state of hydrochloric acid, sulphur being deposited at the same time. In a word, all bodies having much affinity for oxygen cause its decomposition.



$$2\underset{\text{Chloric acid.}}{\left(\left.\begin{matrix}\mathrm{ClO^2}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + 6\underset{\text{Hydrosulphuric acid.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{S}\right)} = 2\underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{Cl}\end{matrix}\right\}\right)} + 3\underset{\text{Sulphur.}}{\left(\left.\begin{matrix}\mathrm{S}\\ \mathrm{S}\end{matrix}\right\}\right)} + 6\underset{\text{Water.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}$$

**Perchloric Acid** ($\mathrm{ClHO^4}$).—In order to prepare this body, one part of chlorate of potassium is distilled with four parts of sulphuric acid, until the drops which distil no longer solidify in the receiver; thus sulphate of potassium, and perchloric acid combined with water of crystallization, are obtained.

$$\underset{\text{Chlorate of potassium.}}{8\left(\left.\begin{matrix}\mathrm{ClO^2}\\ \mathrm{K}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Sulphuric acid.}}{4\left(\left.\begin{matrix}\mathrm{SO^{2\prime\prime}}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{O^2}\right)}$$

$$= \underset{\text{Sulphate of potassium.}}{4\left(\left.\begin{matrix}\mathrm{SO^{2\prime\prime}}\\ \mathrm{K^2}\end{matrix}\right\}\mathrm{O^2}\right)} + \underset{\text{Perchloric acid.}}{4\left(\left.\begin{matrix}\mathrm{ClO^3}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Oxygen.}}{3\left(\left.\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\}\right)} + \underset{\text{Chlorine.}}{2\left(\left.\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right\}\right)}$$

The crystals of hydrated perchloric acid heated to 110° in a retort emit white vapours, which exhale a strong odour of chlorine: these vapours condense in the receiver into a yellowish volatile liquid, which may be obtained colourless by a fresh distillation conducted slowly and carefully.

If the distillation be continued until all the matter passes over, the temperature will rise up to 200°, and an oleaginous liquid will then distil, which, mixed with the volatile liquid, retransforms it into crystals.

The liquid volatile at 110° is normal perchloric acid ($\mathrm{ClHO^4}$). As it strongly attracts atmospheric moisture, and easily explodes, it ought always to be preserved in tubes hermetically sealed.

Normal perchloric acid has a density of 1·782 at 15·5°. Its vapour is colourless and transparent: mixed with air, it emits thick white vapours, owing to its combination with the aqueous vapour contained in the atmosphere.

Poured into water drop by drop, perchloric acid produces effervescence and elevation of the temperature of the liquid. A drop of perchloric acid poured on paper or wood produces immediate explosion with disengagement of light. The action of charcoal is still stronger, giving rise to a detonation, which may be compared to that of chloride of nitrogen.

It also explodes when mixed with anhydrous ether. With alcohol, on the contrary, it mixes tranquilly, the mixture becomes heated, and ether distils.

Applied to the skin, perchloric acid causes painful ulcers, which heal very slowly.

When perchloric acid is heated, it decomposes; and, as the water arising from its decomposition unites with the portion of acid still intact to form the crystallized matter of which we have already spoken, the liquid becomes opaque. On continuing to increase the temperature, a violent explosion occurs; the remaining liquid immediately becomes colourless, and on cooling crystallizes. Perchloric acid decomposes spontaneously, even in the dark, and the tubes containing it all explode at the end of from eight to fifteen days.

When water is added to normal perchloric acid, the liquid becomes heated; and, if the quantity of water be suitable, the mass crystallizes on cooling. The crystals thus obtained, which have been hitherto supposed to be perchloric anhydride, are really the normal acid combined with a molecule of water. Their formula is $(ClHO^4) + aq.$ These crystals deliquesce in air; they melt at 50°; their density when melted is 1·811.

When strongly heated they disengage normal perchloric acid, and there remains in the retort a hydrate richer in water. Continuing the distillation, when the normal acid has passed, there comes over, at about 203°, an oleaginous liquid of a constant composition, which much resembles sulphuric acid. This acid contains 71·6 per cent. of the acid $(ClHO^4)$, and seems to answer to the formula $(ClHO^4)^5 + 11aq.$ The more simple formula $(ClHO^4) + 2aq.$ would require 73·63 per cent. of normal acid, instead of 71·6. The potassic perchlorate being very sparingly soluble in water, perchloric acid precipitates potassic salts from solution.

Perchlorous anhydride is unknown.

## COMBINATIONS OF OXYGEN WITH BROMINE.

The compounds of oxygen and bromine actually known are the hypobromous acid $(BrHO)$, or anhydride $(Br^2O)$, bromic acid $(BrHO^3)$, and perbromic acid $(BrHO^4)$.

**Hypobromous Acid** $\left(\left.\begin{matrix}Br\\H\end{matrix}\right\}O\right)$.—When bromine is poured into an aqueous solution of nitrate of silver a precipitate is formed of bromide of silver, and the supernatant liquid possesses bleaching properties. If this liquid be distilled under the ordinary pressure of the atmosphere it is decomposed, and sets free bromine; but if it be distilled n vacuo it gives a volatile liquid, which bleaches organic substances. The same compound is also obtained by agitating bromine in water with oxide of silver. But, if the oxide of silver be in excess, and the iquor be shaken too long, oxygen will be disengaged, bromide of ilver will be formed, and the fluid would no longer possess bleaching properties.

$$\underset{\text{Hypobromous anhydride.}}{(Br^2O)} + \underset{\text{Oxide of silver.}}{(Ag^2O)} = \underset{\text{Bromide of silver.}}{2\left(\left.\begin{matrix}Ag\\Br\end{matrix}\right\}\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}}$$

The affinity of oxygen for itself is added to that of silver for bromine, and these two forces united determine the double decompo-ition.

Is the body dissolved in the bleaching liquid the preparation of which we have just indicated hypobromous acid $(BrHO)$, or its anhy-ride $(Br^2O)$? This is not known, as we have not yet been able to separate it from the great excess of water with which it is mixed. The fact that it is dissolved would lead us to regard it as hypobromous acid $(BrHO)$; but if we consider that hypochlorous anhydride forms with water a simple solution, and not a hydrate, we shall be tempted to admit that it is the same with hypobromous anhydride.

**Bromic Acid** $\left(\left.\begin{matrix}\mathrm{BrO^2}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)$.—When bromine is made to act on a concentrated solution of potash, a mixture of potassic bromide and bromate is formed. The bromate, which is very sparingly soluble, is precipitated.

$$\underset{\text{Caustic potash.}}{6\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Bromine.}}{3\left(\left.\begin{matrix}\mathrm{Br}\\ \mathrm{Br}\end{matrix}\right\}\right)} = \underset{\text{Bromide of potassium.}}{5\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{Br}\end{matrix}\right\}\right)} + \underset{\text{Potassic bromate.}}{\left(\left.\begin{matrix}\mathrm{BrO^2}\\ \mathrm{K}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Water.}}{3\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}$$

Bromic acid is prepared from bromate of potassium by the same process as chloric acid from chlorate of potassium.

Bromic acid has properties which are similar to those of chloric acid. It is, however, somewhat more stable than the latter acid, and may be heated to a temperature of 30° without decomposing.

**Perbromic Acid** $\left(\left.\begin{matrix}\mathrm{BrO^3}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)$.—Recently M. Kaemmerer has obtained this acid by treating perchloric acid with bromine. The chlorine is simply displaced.

$$\underset{\text{Perchloric acid.}}{2\left(\left.\begin{matrix}\mathrm{ClO^3}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Bromine.}}{\left.\begin{matrix}\mathrm{Br}\\ \mathrm{Br}\end{matrix}\right\}} = \underset{\text{Chlorine.}}{\left.\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right\}} + \underset{\text{Perbromic acid.}}{2\left(\left.\begin{matrix}\mathrm{BrO^3}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}$$

Evaporated in a water-bath, the solution of perbromic acid appears as a syrupy mass, on which sulphuric acid, hydrochloric acid, and sulphurous anhydride have no action. Like perchloric acid, perbromic acid precipitates potassic salts white, but the perbromate of potash is slightly more soluble than the corresponding perchlorate.

## COMBINATIONS OF OXYGEN WITH IODINE.

**Hypo-iodites** $\left(\left.\begin{matrix}\mathrm{I}\\ \mathrm{M'}\end{matrix}\right\}\mathrm{O}\right)$ are very little known. But there is an iodic anhydride ($I^2O^5$), to which an acid ($IH^3O^4$) and a periodic acid ($IH^3O^5$) correspond.

Hypo-iodites appear to be formed when chloride of iodine ($ICl^3$) is dissolved by an alkaline carbonate or a caustic alkali; but they are only stable in presence of a molecule of iodine; when this is taken away they immediately decompose.

**Iodic Anhydride ($I^2O^5$) and Iodic Acid** $\left(\left.\begin{matrix}\mathrm{IO'''}\\ \mathrm{H^3}\end{matrix}\right\}\mathrm{O^3}\right)$.—On boiling one part of iodine in five parts of fuming nitric acid, and letting the liquid cool when the iodine has entirely disappeared, iodic acid is obtained which crystallizes in small pyramids,

It may also be prepared by passing chlorine through water having

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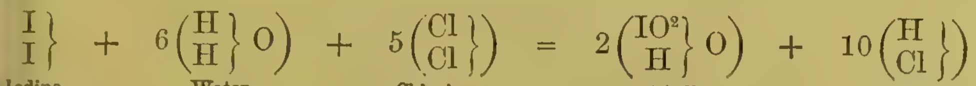
iodine in suspension, and evaporating the solution to crystallization.



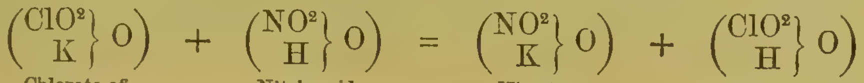
$$\left.\begin{matrix}\mathrm{I}\\\mathrm{I}\end{matrix}\right\} + 6\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right) + 5\left(\left.\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right\}\right) = 2\left(\left.\begin{matrix}\mathrm{IO}^2\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right) + 10\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{Cl}\end{matrix}\right\}\right)$$

Iodine. Water. Chlorine. 1st iodic anhydride. Hydrochloric acid.

Finally, a boiling solution of iodate of potassium may be precipitated by chloride of barium, and afterwards the barytic iodate decomposed by sulphuric acid.

As to potassic iodate, it may be obtained like the corresponding bromate. But it is easier to prepare it by boiling a mixture of 75 parts of chlorate of potassium, 80 of iodine, and 1 of nitric acid in 400 of water, until the chlorine, which is disengaged at the commencement, ceases to come off.

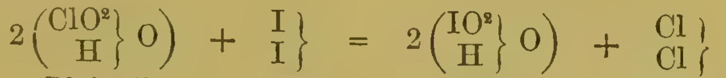
In this reaction, nitric acid at first sets free a little chloric acid.



$$\left(\left.\begin{matrix}\mathrm{ClO}^2\\\mathrm{K}\end{matrix}\right\}\mathrm{O}\right) + \left(\left.\begin{matrix}\mathrm{NO}^2\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right) = \left(\left.\begin{matrix}\mathrm{NO}^2\\\mathrm{K}\end{matrix}\right\}\mathrm{O}\right) + \left(\left.\begin{matrix}\mathrm{ClO}^2\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)$$

Chlorate of potassium. Nitric acid. Nitrate of potassium. Chloric acid.

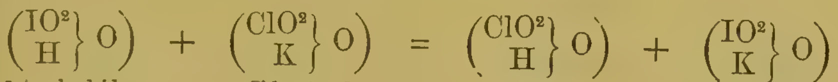
Iodine reacting on this acid transforms it into iodic acid by displacing the chlorine.



$$2\left(\left.\begin{matrix}\mathrm{ClO}^2\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right) + \left.\begin{matrix}\mathrm{I}\\\mathrm{I}\end{matrix}\right\} = 2\left(\left.\begin{matrix}\mathrm{IO}^2\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right) + \left.\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right\}$$

Chloric acid. Iodine. 1st iodic anhydride. Chlorine.

Iodic acid, or rather its first anhydride, reacts on a new portion of potassic chlorate, and produces iodate of potassium and chloric acid.



$$\left(\left.\begin{matrix}\mathrm{IO}^2\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right) + \left(\left.\begin{matrix}\mathrm{ClO}^2\\\mathrm{K}\end{matrix}\right\}\mathrm{O}\right) = \left(\left.\begin{matrix}\mathrm{ClO}^2\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right) + \left(\left.\begin{matrix}\mathrm{IO}^2\\\mathrm{K}\end{matrix}\right\}\mathrm{O}\right)$$

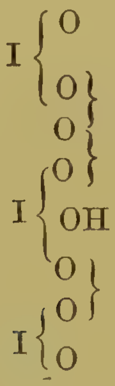
1st anhydride of iodic acid. Chlorate of potassium. Chloric acid. Iodate of potassium.

The iodine transforms this second quantity of chloric acid into iodic acid as it did the first, and this series of double decompositions continues until the whole of the chlorate of potassium is transformed into iodate.

When iodic acid has been prepared by deposition from a cold concentrated solution, crystals are obtained which have the composition of the first iodic anhydride $\left(\left.\begin{matrix}\mathrm{IO}^2\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)$. On dissolving these crystals in sulphuric acid diluted with four parts of water, a liquid is obtained which leaves a white product corresponding to the formula $\left(\left.\begin{matrix}\mathrm{IO}^2\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)$.

The first iodic anhydride maintained at 130° until it no longer loses weight is transformed into an anhydride ($\mathrm{I^3HO^8}$) of the unknown triiodic acid ($\mathrm{I^3H^5O^{10}}$).

This latter anhydride may be represented by the rational formula—



$$\begin{array}{l} I\left\{\begin{matrix}O\\ \\ O\end{matrix}\right. \\ \quad\left.\begin{matrix}O\\O\\O\end{matrix}\right\} \\ I\left\{\begin{matrix}O\\OH\\O\end{matrix}\right. \\ \quad\left.\begin{matrix}O\\O\end{matrix}\right\} \\ I\left\{\begin{matrix}O\\O\end{matrix}\right. \end{array}$$

and the unknown normal acid to which it corresponds, by a similar formula, but in which the two O at the extremities will be replaced by two atoms of hydroxyl.

Heated to 170°, iodic acid is transformed into iodic anhydride ($I^2O^5$).

Anhydrous alcohol dissolves neither iodic acid nor its anhydrides.

Iodic acid combines with nitric, phosphoric, boric, and sulphuric acids, giving crystalline compounds.

Iodic acid is soluble in water: it reddens litmus and decolorizes it after a time; heated to a temperature lower than redness, it decomposes into iodine and oxygen without giving periodic acid. It is an oxidizing body: treated by hydrosulphuric acid or sulphurous anhydride, it decomposes and gives a deposit of iodine.

$$\underset{\text{1st iodic anhydride.}}{2\left(\left.\begin{matrix}IO^2\\H\end{matrix}\right\}O\right)} + \underset{\text{Sulphurous anhydride.}}{5\left(SO^2\right)} + \underset{\text{Water.}}{4\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Iodine.}}{\left.\begin{matrix}I\\I\end{matrix}\right\}} + \underset{\text{Sulphuric acid.}}{5\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)}$$

Hydrochloric acid immediately decomposes iodic acid, disengaging chlorine.

$$\underset{\text{Iodic anhydride.}}{\left(I^2O^5\right)} + \underset{\text{Hydrochloric acid.}}{10\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\text{Iodine.}}{\left.\begin{matrix}I\\I\end{matrix}\right\}} + \underset{\text{Chlorine.}}{5\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}\right)} + \underset{\text{Water.}}{5\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

**Periodic Acid** ($IH^3O^5$).—Periodic acid may be prepared like perbromic acid; that is to say, by making iodine act on perchloric acid. It may also be obtained by the following process:

A current of chlorine is transmitted through a solution of iodate of sodium containing an excess of alkali, when an insoluble sodic periodate is precipitated. This precipitate dissolved in nitric acid gives, with nitrate of silver, a white precipitate of periodate of silver, of which the formula is—

$$I'''\left\{\begin{array}{l}OAg\\O\\OH\\O\\OAg\end{array}\right. + 2aq.$$

This salt is dissolved in boiling nitric acid, and on cooling the liquor gives crystals whose formula is $(IAgO^4)$.

These crystals treated by cold water are transformed into an insoluble diargentic periodate $(IHAg^2O^5)$, and free iodic acid which dissolves.

$$\underset{\substack{\text{Periodate of}\\\text{silver.}}}{2(IAgO^4)} + \underset{\text{Water.}}{2(H^2O)} = \underset{\substack{\text{Diargentic}\\\text{periodate.}}}{(IAg^2HO^5)} + \underset{\substack{\text{Periodic}\\\text{acid.}}}{(IH^3O^5)}$$

As we see from the different reactions just explained, normal periodic acid is triatomic, and its formula is $(IH^3O^5)$. The acid $(IHO^4)$ would only be the first anhydride of this normal acid; it is unknown in a free state, but salts are known which correspond to it.

Periodic acid $(IH^3O^5)$ crystallizes with two molecules of water. It melts at 130°. At about 200° it loses water, and is transformed into oxygen and iodic acid. Hydrosulphuric acid and sulphurous anhydride easily destroy it.

With salts of soda, periodic acid gives a precipitate of disodic periodate.

## SULPHUR.

Atomic weight = 32. Molecular weight = 64.

Sulphur is procured from certain volcanic countries where it exists native, especially from Sicily. There are mines elsewhere, but they are not yet worked.

In Sicily, sulphur is separated from the earthy matter either by melting it, if the mineral be rich enough, or otherwise by distilling. After importation, the sulphur is refined by a second distillation performed in a retort which communicates with a large brickwork chamber. The retort is so disposed that fresh quantities of sulphur can be introduced into it without arresting the operation. If the process be conducted with sufficient rapidity to distill 1800 kilogrammes of sulphur in twenty-four hours, the walls of the chamber become so hot that the sulphur is kept in a liquid state. On taking it out, it is poured into wooden moulds and sold in rolls. If, on the contary, the operation be conducted so slowly that the weight of sulphur distilled in twenty-four hours does not exceed 300 kilogrammes, the metalloid is solidified in the chamber, and as air interposes between its molecules at the moment of solidification, it is sublimated in the form of a powder known as "flowers of sulphur."

Sulphur is yellow, solid at the ordinary temperature, fusible at 114° and volatile at 440°. It is tasteless and inodorous; its density is equal to 2·08, its vapour density is represented by the number 6·666 at 500°, and by 2·222 at 1000°.

Water does not dissolve sulphur; alcohol and ether dissolve it very sparingly; its best solvent is sulphide of carbon.

By evaporating its solution in sulphide of carbon, we obtain the sulphur crystallized in octahedra of the fourth system; it is under this form that it is found in a natural state. By means of fusion it crystallizes in prisms of the fifth system.

At the ordinary temperature the prismatic crystals fall to powder, which appears under the microscope to be formed of small octahedra. At about 114° the contrary takes place; the octahedral crystals become prismatic. These two facts show that the difference of crystalline form which we remark in sulphur is owing to the temperature at which the crystallization took place.

We have already said that sulphur melts at 114°; it then constitutes a yellow and very fluid liquid: at 140° its colour becomes deeper, at 160° it is brown and viscid, at 230° its viscidity is such that the vessel containing it may be inverted without the sulphur running out; above 230° it regains its fluidity, but retains its brown colour up to 440°, when it commences to boil.

If sulphur be heated to nearly its boiling point, and then suddenly cooled, when completely cold it remains soft for a time, but gradually regains its consistency, and by heating it to about 96° it can be made to regain it immediately. M. Regnault, to whom we owe the knowledge of this fact, also says that the passage of sulphur from a soft to a hard state is always accompanied by the disengagement of heat.

Sulphur is inflammable; it burns in air with a blue flame and emits an odour of sulphurous anhydride, which is well known.

It combines very readily with chlorine, and has such an affinity for phosphorus that, except under water, a mixture of these two bodies cannot be heated for fear of an explosion.

Almost all metals, carbon, and in general bodies which readily unite with oxygen, have a great affinity for sulphur. But hydrogen only combines with it at red heat and with great difficulty.

When sulphur is heated to a high temperature and then suddenly cooled, we have seen that it remains soft. If it be thus treated seven times successively it acquires a brown colour, which it retains in the solid state. Treated by sulphide of carbon, it then leaves a reddish residue, which is only sulphur in a particular allotropic state. Thus modified, sulphur is entirely insoluble. It returns to its ordinary state when heated to 100°, or when brought into contact with hydrosulphuric acid or alkaline sulphides. It acquires, on the contrary, a greater stability when chloride of sulphur is made to act on it.

On decomposing chloride of sulphur by water the same insoluble sulphur is obtained, but in a more stable form. When, on the contrary, the polysulphides are decomposed by acids, crystallizable sulphur is obtained. M. Berthelot thought he could deduce from these facts that sulphur enters in the amorphous state into the compounds where it is electro-positive, and in the crystallizable state into the compounds where it is electro-negative. But M. Cloez has shown that from one compound, chloride of sulphur, it is possible to extract, by means of water, either a soluble or an insoluble sulphur, according to the rapidity of the reaction. This experiment, and several others equally important which we owe to this able chemist, have upset the preceding theory.

M. Berthelot thinks that when melted sulphur is heated to 440° it is entirely modified, and that if, by steeping, sulphur is never obtained in an insoluble state, it is owing to an inverse modification which is produced during the cooling. In fact he has remarked: 1st, that the more sudden the cooling, the greater is the proportion of the insoluble sulphur that is obtained; 2nd, that on mixing with the water certain bodies, such as nitric acid, which have the property of rendering the insoluble sulphur stable, hardly any crystallizable sulphur is obtained.

Sulphur when heated to 440° being in its insoluble modification, it is probable that at 500°, that is to say, at an approximate temperature to 440°, it exists in the same state. As at 500° the vapour density of sulphur is 6·666, which gives 192 as the molecular weight of this body and $\left.\begin{matrix}S^3\\S^3\end{matrix}\right\}$ as its formula, we may conclude that there exist two varieties of sulphur: crystallizable sulphur, the molecular weight of which is 64, and which answers to the formula $\left.\begin{matrix}S\\S\end{matrix}\right\}$; and insoluble sulphur, the molecular weight of which is 192, and its formula $\left.\begin{matrix}S^3\\S^3\end{matrix}\right\}$.

Sulphur is employed in medicine, either in its metalloid state or in combination. It is parasiticide, and it is for this property that it is chiefly used. Some soluble sulphides are also used to stimulate the functions of the skin.

The sulphur used in pharmacy is usually the flowers of sulphur, which must be washed to remove the sulphurous anhydride with which it is always mixed.

## COMBINATIONS OF SULPHUR WITH THE METALLOIDS PREVIOUSLY STUDIED.

### Combinations of Sulphur with Hydrogen.

**Hydrosulphuric Acid** $\left(\left.\begin{matrix}H\\H\end{matrix}\right\}S\right)$ (Sulphuretted Hydrogen). Hydrosulphuric acid is prepared by making cold sulphuric or hydrochloric acid act on sulphide of iron, or by heating sulphide of antimony with hydrochloric acid.

$$\text{1st.}\quad \underset{\text{Sulphide of iron.}}{\left(\mathrm{FeS}\right)} + \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}\mathrm{SO^{2\prime\prime}}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{O^2}\right)} = \underset{\text{Sulphate of iron.}}{\left(\left.\begin{matrix}\mathrm{SO^{2\prime\prime}}\\ \mathrm{Fe^{\prime\prime}}\end{matrix}\right\}\mathrm{O^2}\right)} + \underset{\text{Hydrosulphuric acid.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{S}\right)}$$

$$\text{2nd.}\quad \underset{\text{Sulphide of antimony.}}{\left(\mathrm{Sb^2S^3}\right)} + \underset{\text{Hydrochloric acid.}}{6\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{Cl}\end{matrix}\right\}\right)} = \underset{\text{Terchloride of antimony.}}{2\left(\mathrm{SbCl^3}\right)} + \underset{\text{Hydrosulphuric acid.}}{3\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{S}\right)}$$

Hydrosulphuric acid is gaseous at ordinary temperatures. A pressure of 17 to 18 atmospheres liquefies it. Its density in the gaseous state is 1·1912, and in the liquid state 0·9; water dissolves about three times its volume.

Hydrosulphuric acid is a weak acid, and scarcely reddens litmus.

It burns in air with a dull flame, forming water and sulphurous anhydride.

$$\underset{\text{Hydrosulphuric acid.}}{2\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{S}\right)} + \underset{\text{Oxygen.}}{3\left(\left.\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\}\right)} = \underset{\text{Water.}}{2\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Sulphurous anhydride.}}{2\left(\mathrm{SO^2}\right)}$$

When exposed to air, the aqueous solution of sulphuretted hydrogen is decomposed. The sulphur is displaced by oxygen and is deposited in white flakes.

$$\underset{\text{Hydrosulphuric acid.}}{2\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{S}\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\}} = \underset{\text{Water.}}{2\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Sulphur.}}{\left.\begin{matrix}\mathrm{S}\\ \mathrm{S}\end{matrix}\right\}}$$

In contact with porous bodies, this solution absorbs oxygen and forms sulphuric acid.

$$\underset{\text{Hydrosulphuric acid.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{S}\right)} + \underset{\text{Oxygen.}}{2\left(\left.\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\}\right)} = \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}\mathrm{SO^{2\prime\prime}}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{O^2}\right)}$$

It has been observed that woollen goods steeped in a solution of hydrosulphuric acid fall to rags. This is owing to the corrosive action of the sulphuric acid which is formed.

Sulphuretted hydrogen is decomposed by chlorine, bromine, and iodine, with the deposition of sulphur and formation of a hydrogenized compound of the metalloid employed.

Hydrosulphuric acid precipitates the soluble salts of lead black; a sulphide of the metal is produced, and an acid corresponding to the salt employed.

$$\underset{\text{Salt of lead.}}{\left(\mathrm{Pb^{\prime\prime}R^{\prime\prime}}\right)} + \underset{\text{Hydrosulphuric acid.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{S}\right)} = \underset{\text{Sulphate of lead.}}{\left(\mathrm{Pb^{\prime\prime}S}\right)} + \underset{\text{Acid corresponding to the salt of lead.}}{\left(\mathrm{R^{\prime\prime}H^2}\right)}$$

Hydrosulphuric acid has a very disagreeable odour resembling rotten eggs. It is poisonous when breathed, but large quantities of its solution in water may be drank without danger. It is very little used in medicine, except as an element of certain mineral waters.

Sulphuretted hydrogen is analyzed in the same manner as hydrochloric acid. But, instead of sodium, a piece of tin is placed in the curved glass. Sodium could only be substituted for the half of the hydrogen of this acid.

Sulphuretted hydrogen contains a volume of hydrogen equal to its own.

| | |
|---|---|
| If from the density of hydrosulphuric acid . . | 1·1912 |
| we subtract the density of the hydrogen . . | 0·0692 |
| there remains . . . . . . . . . . . . | 1·1220 |

which is evidently equal to half the density of the vapour of sulphur at 1000°. Two volumes of hydrosulphuric acid, therefore, contain one volume of sulphur vapour and two volumes of hydrogen condensed into two volumes.

From this volumetric composition we arrive at its composition by weight. We have first—

$$1{\cdot}1912 : 0{\cdot}0692 :: 100 : x; \text{ that is to say, } x = \frac{6{\cdot}92}{1{\cdot}1912} = 5{\cdot}809$$

Secondly—

$$1{\cdot}1912 : 1{\cdot}122 :: 100 : x; \text{ that is to say, } x = \frac{112{\cdot}2}{1{\cdot}1912} = 94{\cdot}191$$

100 parts of hydrosulphuric acid, therefore, contain

| | |
|---|---|
| Sulphur . . . . . . . . . . . . | 94·191 |
| Hydrogen . . . . . . . . . . . | 5·809 |
| | 100·000 |

**Bisulphide of Hydrogen** $\left(\left.\begin{matrix}H\\H\end{matrix}\right\}S^2\right)$.—Bisulphide of hydrogen is obtained by pouring drop by drop a solution of bisulphide of calcium into hydrochloric acid.

$$\underset{\text{Bisulphide of calcium.}}{\left(Ca''S^2\right)} + \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\text{Chloride of calcium.}}{\left(\left.\begin{matrix}Ca''\\Cl^2\end{matrix}\right\}\right)} + \underset{\text{Bisulphide of hydrogen.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}S^2\right)}$$

If the operation be reversed, that is to say, if the hydrochloric acid be poured into the solution of bisulphide of calcium, the bisulphide of hydrogen, finding itself at the time of its formation in contact with an excess of sulphide of calcium, will decompose, and hydrosulphuric acid and sulphur will be obtained. Bisulphide of hydrogen possesses properties analogous to those of oxygenated water.

MEDICINE

### COMBINATIONS OF SULPHUR WITH OXYGEN.

The compounds of sulphur with oxygen are the following:—

Sulphurous anhydride ($SO^2$).
Sulphuric anhydride ($SO^3$) and sulphuric acid ($SH^2O^4$).

The hyposulphites correspond to the hyposulphurous anhydride and to hyposulphurous acid (unknown).

Dithionic acid ($S^2H^2O^6$).
Trithionic acid ($S^3H^2O^6$).
Tetrathionic acid ($S^4H^2O^6$).
Pentathionic acid ($S^5H^2O^6$).

The anhydrides which correspond to these four acids have not hitherto been prepared.

**Sulphurous Anhydride** ($SO^2$).—This body is prepared either by burning sulphur in oxygen, or by heating the metalloid with an oxygen compound of slight stability, such as binoxide of manganese, or by deoxidizing sulphuric acid by means of mercury or copper, and heat.

$$\underset{\text{Sulphuric acid.}}{2\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Copper.}}{Cu''} = \underset{\text{Sulphate of copper.}}{\left(\left.\begin{matrix}SO^{2''}\\Cu''\end{matrix}\right\}O^2\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Sulphurous anhydride.}}{\left(SO^2\right)}$$

Sulphurous anhydride is gaseous; it is liquefied at −10°; the vaporization of the liquid acid causes the thermometer to descend to −60°.

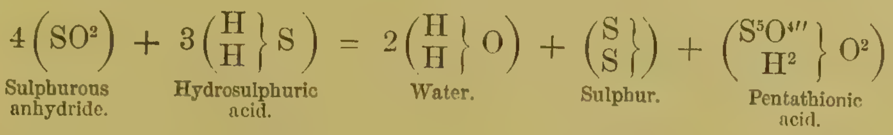
In the gaseous state its density is 2·247; water dissolves fifty times its volume: this solution, left in the air, absorbs oxygen, and sulphuric acid is formed.

The solution of sulphurous anhydride, when sufficiently cooled, deposits crystalline compounds. Three have been described; they have for formula ($SO^2 + 14H^2O$); ($SO^2 + 9H^2O$); ($SO^2 + H^2O$). The last may be considered as normal sulphurous acid, and be written $\left(\left.\begin{matrix}SO''\\H^2\end{matrix}\right\}O^2\right)$. It is, nevertheless, more probable that its water acts as water of crystallization.

Sulphurous anhydride is colourless and has a pungent odour. When breathed it excites coughing, but is not dangerous, unless it forms a large proportion of the atmosphere. It does not burn and does not support combustion, but it combines directly with oxygen in presence of spongy platinum, giving rise to sulphuric anhydride.

$$\underset{\text{Sulphurous anhydride.}}{2\left(SO^2\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} = \underset{\text{Sulphuric anhydride.}}{2\left(SO^3\right)}$$

Sulphurous anhydride and hydrosulphuric acid decompose each other, forming water and pentathionic acid, sulphur being deposited.

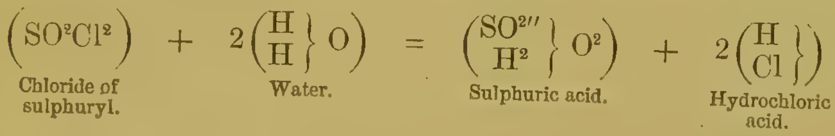


$$\underset{\substack{\text{Sulphurous}\\\text{anhydride.}}}{4\left(SO^2\right)} + \underset{\substack{\text{Hydrosulphuric}\\\text{acid.}}}{3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}S\right)} = \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Sulphur.}}{\left(\left.\begin{matrix}S\\S\end{matrix}\right\}\right)} + \underset{\substack{\text{Pentathionic}\\\text{acid.}}}{\left(\left.\begin{matrix}S^5O^{4''}\\H^2\end{matrix}\right\}O^2\right)}$$

Sulphurous anhydride is a powerful reducing agent; it takes oxygen from all substances which are feebly united to it. In presence of water it liberates chlorine, bromine, and iodine from their compounds. The water acts in this case by its oxygen oxidizing the sulphurous anhydride, while its hydrogen unites with the chlorine, bromine, or iodine, to form a hydracid.

Sulphurous anhydride bleaches vegetable substances, but does not greatly alter them. By treating the bodies thus bleached by a base we cause their original colour to reappear, or, rather, the shade they would have taken on contact with the base employed. This property is utilized in the arts for bleaching straw bonnets or hats.

In the direct light of the sun, sulphurous anhydride combines with its volume of chlorine, and the volume of the gaseous mixture diminishes by half. The compound which arises has for formula ($SO^2Cl^2$). It was formerly called chlorosulphuric acid, but now its name is chloride of sulphuryl. In presence of water it changes into hydrochloric and sulphuric acids.



$$\underset{\substack{\text{Chloride of}\\\text{sulphuryl.}}}{\left(SO^2Cl^2\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)}$$

When iodine acts on sulphurous anhydride, it forms a similar compound ($SO^2I^2$), which possesses analogous properties.

To determine the composition of sulphurous anhydride, an excess of sulphur is burned in a known volume of oxygen until the whole of this gas is consumed. Then it is observed that the sulphurous anhydride which is formed, occupies the same volume as the oxygen which served for the combustion.

| | |
|---|---|
| If from the density of sulphurous anhydride . . . | 2·247 |
| we subtract the density of the oxygen . . . . . | 1·105 |
| there remains . . . . . . . . . . . . . . | 1·142 |

a number which evidently represents half the vapour density of sulphur at 1000°.

Two volumes of sulphurous anhydride, therefore, contain two volumes of oxygen and one volume of sulphur vapour combined with a contraction of $\frac{1}{3}$. From the knowledge of this volumetric composition, it is easy to calculate its composition by weight.

Sulphurous anhydride has no special use in medicine.

**Sulphuric Acid** $\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)$.—In manufactures this acid is prepared in large leaden chambers by making nitric acid, water, and air act on sulphurous anhydride. This latter body is obtained by the direct combustion of sulphur.

The sulphurous anhydride and nitric acid are transformed into hyponitric and sulphuric acids. Then water divides the hyponitric acid into nitric acid and nitric oxide, and the nitric oxide absorbs oxygen from the air to reform hyponitric acid. Finally, all the nitric acid decomposed is reformed. The cycle of the preceding reactions then recommences, and this may be continued indefinitely, allowing for the inevitable losses which every large manufacture involves. The following equations express these reactions:—

1st. $$\underset{\text{Sulphurous anhydride.}}{\left(SO^2\right)} + \underset{\text{Nitric acid.}}{2\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)} = \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Hyponitric acid.}}{2(NO^2)}$$

2nd. $$\underset{\text{Hyponitric acid.}}{3\left(NO^2\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Nitric acid.}}{2\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)} + \underset{\text{Nitric oxide.}}{\left(NO\right)}$$

3rd. $$\underset{\text{Nitric oxide.}}{2\left(NO\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} = \underset{\text{Hyponitric acid.}}{2\left(NO^2\right)}$$

As an excess of water is necessary for the success of the operation, the sulphuric acid as it leaves the leaden chamber is always largely diluted. It is concentrated in leaden vessels until it reaches 59° according to Baumé's scale of acid weights (sp. gr. 1·729), and the concentration is then completed in glass or platinum retorts.

Sulphuric acid may also be obtained in small quantities by boiling sulphur with nitric acid.

$$\underset{\text{Sulphur.}}{\left.\begin{matrix}S\\S\end{matrix}\right\}} + \underset{\text{Nitric acid.}}{4\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)} = \underset{\text{Sulphuric acid.}}{2\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Nitric oxide.}}{4(NO)}$$

Sulphuric acid is an oily liquid of a density of 1·848 at 15°; it boils at 325°, and is solidified at $-35°$. It has neither colour nor smell, but has a strongly acid taste. When touched it disorganizes the skin, giving a saponaceous feeling.

Sulphuric acid combines directly with water with considerable disengagement of heat, and a contraction of volume. According to the proportion of water, two hydrates may be formed—

$$\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right) + \text{Aq. and } \left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right) + 2\text{ Aq.}$$

The hydrogen of the water combined can never be replaced by metals; this indicates that the water acts a part analogous to that of water of crystallization. The first of these hydrates is crystallizable; in the case of the second, we recognize that it has a definite composition, because the maximum of contraction is obtained when sulphuric acid is mixed with water in the proportion of one molecule of acid to two molecules of water.

The affinity of sulphuric acid for water is such that it carbonizes organic substances, causing the formation of water at the expense of the oxygen and hydrogen contained in these substances. It is a very powerful acid, decomposing most salts derived from other acids and liberating these latter; phosphoric, boracic, and silicic acids alone can decompose the sulphates by the aid of heat, on account of their greater stability. (*See* Berthollet's laws).

Sulphuric acid forms two series of salts: the one neutral, represented by the general formula $\left(\left.\begin{matrix}SO^{2''}\\R'^2\end{matrix}\right\}O^2\right)$; the other acid answering to the formula $\left(\left.\begin{matrix}SO^{2''}\\R'\\H\end{matrix}\right\}O^2\right)$.*

To analyze sulphuric acid we proceed as follows:

1st. An excess of sulphuric acid is poured on a known weight of pure oxide of barium. Sulphate of barium and water are formed.

$$\underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)}+\underset{\text{Oxide of barium (baryta).}}{\left(Ba''O\right)}=\underset{\text{Sulphate of barium.}}{\left(\left.\begin{matrix}SO^{2''}\\Ba''\end{matrix}\right\}O^2\right)}+\underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

The water and the excess of acid are driven off by evaporation, and the sulphate of barium is weighed. Let P be the weight of this salt, and *p* the weight of barium contained in the baryta employed (the composition of baryta is supposed to be known); the weight of barium contained in 100 parts of the sulphate will be known by the help of the proportion—$P : p :: 100 : x$.

2nd. A known weight of sulphur $q$ is placed in a globe with an excess of nitric acid, and the whole is heated, care being taken to place a refrigerator above the globe, in order that all the vapours which there form may be condensed and continually flow back again into the globe.

When all the sulphur has disappeared the operation is arrested, and the contents of the globe are precipitated by chloride of barium; all the sulphuric acid is thus transformed into insoluble sulphate of barium, according to the equation—

$$\underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)}+\underset{\text{Chlorate of barium.}}{\left(\left.\begin{matrix}Ba''\\Cl^2\end{matrix}\right\}\right)}=\underset{\text{Sulphate of barium.}}{\left(\left.\begin{matrix}SO^{2''}\\Ba''\end{matrix}\right\}O^2\right)}+\underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)}$$

The salt is collected on a filter, well washed, dried, and weighed. Let $P''$ be its weight, and $p'$ the weight of the barium it contains. $P''-p'$ represents the united weights of the sulphur and oxygen. On subtracting the weight of the sulphur *q*, there remains that of the oxygen, which is thus determined. We learn in this manner that 100 parts of sulphate of barium contain—

---

* R′ may be any monatomic positive radical.

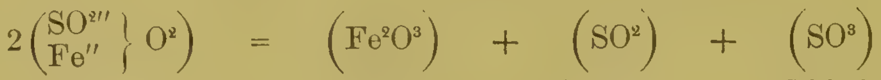
| | |
|---|---|
| Barium | 58·79 |
| Sulphur | 13·74 |
| Oxygen | 27·47 |
| | 100·00 |

3rd. A known weight of concentrated sulphuric acid is precipitated by chloride of barium, and the sulphate of barium produced is weighed. From this weight, that of the oxygen and sulphur which the salt contains is calculated. Now as all this sulphur and oxygen will be found in the sulphuric acid employed, it suffices to subtract the amount of their weight from that of this acid in order to know the quantity of hydrogen contained in the latter.

By means of three proportions the composition found is then transformed into centesimal composition.

In medicine, sulphuric acid largely diluted is used internally as an astringent, and externally for stimulating foot baths. It is also employed as a caustic.

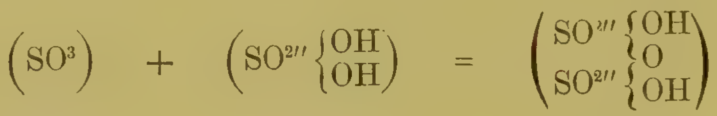
**Nordhausen Sulphuric Acid** $\left(\begin{array}{l} SO^{2''}\left\{\begin{array}{l}OH\\ O\end{array}\right. \\ SO^{2''}\left\{OH\right.\end{array}\right)$ (DISULPHURIC ACID.) — On calcining in a closed vessel protosulphate of iron as dry as it can be obtained on a large scale, sesquioxide of iron is formed, and sulphurous anhydride is disengaged, and also sulphuric anhydride combined with the small quantity of water which the salt still contained.



$$2\left(\left.\begin{array}{l}SO^{2''}\\ Fe''\end{array}\right\} O^{2}\right) = \left(Fe^{2}O^{3}\right) + \left(SO^{2}\right) + \left(SO^{3}\right)$$

Protosulphate of iron. Sesquioxide of iron. Sulphurous anhydride. Sulphuric anhydride.

The sulphuric anhydride, received in vessels full of ordinary sulphuric acid, combines with this acid, giving rise to disulphuric acid.



$$\left(SO^{3}\right) + \left(SO^{2''}\left\{\begin{array}{l}OH\\ OH\end{array}\right.\right) = \left(\begin{array}{l} SO^{2''}\left\{\begin{array}{l}OH\\ O\end{array}\right. \\ SO^{2''}\left\{OH\right.\end{array}\right)$$

Sulphuric anhydride. Sulphuric acid. Disulphuric acid.

Disulphuric acid is stronger than ordinary sulphuric acid; it fumes in air, and when heated to about 30° it separates into sulphuric anhydride which is given off, and sulphuric acid which remains in the apparatus. The preceding equation reversed, explains this reaction.

When the acid sulphates are heated they lose water, and are transformed into neutral disulphates (neutral salts of the disulphuric acid).

$$\underset{\text{Acid sulphate of sodium.}}{2\left(SO^2\left\{\begin{matrix}ONa\\OH\end{matrix}\right.\right)} = \underset{\text{Neutral disulphate of sodium.}}{\left(\begin{matrix}SO^{2\prime\prime}\left\{\begin{matrix}ONa\\O\end{matrix}\right.\\SO^{2\prime\prime}\left\{\begin{matrix}\\ONa\end{matrix}\right.\end{matrix}\right)} + \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O}$$

At an elevated temperature these salts are resolved into neutral sulphates and sulphuric anhydride:

$$\underset{\text{Neutral disulphate of sodium.}}{\left(\begin{matrix}SO^{2\prime\prime}\left\{\begin{matrix}ONa\\O\end{matrix}\right.\\SO^{2\prime\prime}\left\{\begin{matrix}\\ONa\end{matrix}\right.\end{matrix}\right)} = \underset{\text{Neutral sulphate of sodium.}}{\left(SO^2\left\{\begin{matrix}ONa\\ONa\end{matrix}\right.\right)} + \underset{\text{Sulphuric anhydride.}}{SO^3}$$

Disulphuric acid dissolves indigo more readily than sulphuric acid. With an excess of base, Nordhausen sulphuric acid gives neutral sulphates.

The composition of this acid is determined by transforming it into sulphate of barium, exactly as with ordinary sulphuric acid.

**Sulphuric Anhydride** $SO^3$.—This body is obtained either by gently heating disulphuric acid, or by calcining a bisulphate, or by passing a mixture of sulphurous anhydride and oxygen over some spongy platinum gently heated.

It is crystallized in silky needles, fusible at 25°, volatile at 35°, and has a great affinity for water. Baryta burns in its vapour, producing sulphate of barium.

$$\underset{\text{Sulphuric anhydride.}}{(SO^3)} + \underset{\text{Baryta.}}{(Ba''O)} = \underset{\text{Sulphate of barium.}}{(Ba''SO^4)}$$

In order to determine its composition it is combined with water, and the acid produced is precipitated by chloride of barium. From the weight of the sulphate of barium obtained, that of the sulphur contained in the salt is deduced, and then on deducting this weight from that of the sulphuric anhydride employed, we learn the quantity of oxygen contained in the compound.

**Thionic Series.**—This series contains four acids whose anhydrides are unknown: they are dithionic or hyposulphuric acid ($S^2H^2O^6$), whose anhydride would be ($S^2O^5$).

Trithionic or monosulphuretted hyposulphuric acid ($S^3H^2O^6$), whose anhydride would be ($S^3O^5$).

Tetrathionic or bisulphuretted hyposulphuric acid ($S^4H^2O^6$), whose anhydride would be ($S^4O^5$).

Pentathionic or trisulphuretted hyposulphuric acid ($S^5H^2O^6$), whose anhydride would be ($S^5O^5$).

These four acids all contain the same quantity of oxygen, and only differ in the quantity of sulphur which each term of the series contains, viz., one more atom than that which precedes it, and one less than that which follows.

**Dithionic Acid** ($S^2H^2O^6$).—If a current of sulphurous anhydride be transmitted through water in which finely-powdered binoxide of manganese is suspended, a mixture of sulphate and dithionate of manganese is formed.

$$\underset{\text{Sulphurous anhydride.}}{(SO^2)} + \underset{\text{Binoxide of manganese.}}{(MnO^2)} = \underset{\text{Manganous sulphate.}}{\left(\left.\begin{matrix}SO^{2''}\\ Mn''\end{matrix}\right\} O^2\right)}$$

$$\underset{\text{Sulphurous anhydride.}}{2(SO^2)} + \underset{\text{Binoxide of manganese.}}{(MnO^2)} = \underset{\text{Dithionate of manganese.}}{\left(\left.\begin{matrix}S^2O^{4''}\\ Mn''\end{matrix}\right\} O^2\right)}$$

An excess of hydrate of barium is poured into the solution containing these two salts. The manganese is precipitated in the state of hydrate, while the sulphate and dithionate of barium are produced.

$$\underset{\text{Manganous sulphate.}}{\left(\left.\begin{matrix}SO^2\\ Mn''\end{matrix}\right\} O^2\right)} + \underset{\text{Hydrate of barium.}}{\left(\left.\begin{matrix}Ba''\\ H^2\end{matrix}\right\} O^2\right)} = \underset{\text{Sulphate of barium.}}{\left(\left.\begin{matrix}SO^{2''}\\ Ba''\end{matrix}\right\} O^2\right)} + \underset{\text{Manganous hydrate.}}{\left(\left.\begin{matrix}Mn''\\ H^2\end{matrix}\right\} O^2\right)}$$

$$\underset{\text{Manganous dithionate.}}{\left(\left.\begin{matrix}S^2O^{4''}\\ Mn''\end{matrix}\right\} O^2\right)} + \underset{\text{Hydrate of barium.}}{\left(\left.\begin{matrix}Ba''\\ H^2\end{matrix}\right\} O^2\right)} = \underset{\text{Dithionate of barium.}}{\left(\left.\begin{matrix}S^2O^{4''}\\ Ba''\end{matrix}\right\} O^2\right)} + \underset{\text{Manganous hydrate.}}{\left(\left.\begin{matrix}Mn''\\ H^2\end{matrix}\right\} O^2\right)}$$

The sulphate of barium is precipitated with the hydrate of manganese, and the filtered liquid contains dithionate of barium alone. The solution is concentrated, and sulphuric acid is added drop by drop until the last drop no longer produces any precipitate. The barium is eliminated in the state of sulphate, and the dithionic acid is set free.

$$\underset{\text{Dithionate of barium.}}{\left(\left.\begin{matrix}S^2O^{4''}\\ Ba''\end{matrix}\right\} O^2\right)} + \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2''}\\ H^2\end{matrix}\right\} O^2\right)} = \underset{\text{Sulphate of barium.}}{\left(\left.\begin{matrix}SO^{2''}\\ Ba''\end{matrix}\right\} O^2\right)} + \underset{\text{Dithionic acid.}}{\left(\left.\begin{matrix}S^2O^{4''}\\ H^2\end{matrix}\right\} O^2\right)}$$

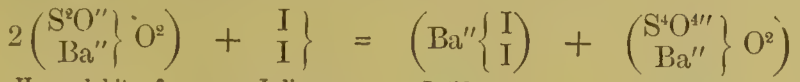
The liquid is then filtered and concentrated until its density is 1·347.

Dithionates when highly calcined disengage sulphurous anhydride, and are converted into sulphates.

$$\underset{\text{Dithionate of barium.}}{\left(\left.\begin{matrix}S^2O^{4''}\\ Ba''\end{matrix}\right\} O^2\right)} = \underset{\text{Sulphurous anhydride.}}{(SO^2)} + \underset{\text{Sulphate of barium.}}{\left(\left.\begin{matrix}SO^{2''}\\ Ba''\end{matrix}\right\} O^2\right)}$$

**Trithionic Acid** $\left(\left.\begin{matrix}S^3O^{4''}\\ H^2\end{matrix}\right\} O^2\right)$.—If flowers of sulphur be digested for several days in a solution of bisulphite of barium at a temperature of 30°, trithionate of barium is formed; from which trithionic acid may be extracted by means of sulphuric acid, in the same way as dithionic acid.

**Tetrathionic Acid** $\left(\left.\begin{matrix}S^4O^{4''}\\ H^2\end{matrix}\right\} O^2\right)$.—This acid is prepared by adding iodine to a solution of hyposulphite of barium until the liquid has a persistent colour, and by decomposing by sulphuric acid the tetrathionate of barium which is formed in the reaction. The formation of this latter salt is explained by the following equation:

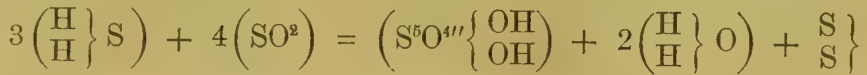


$$2\left(\left.\begin{matrix}S^2O''\\Ba''\end{matrix}\right\}O^2\right) + \left.\begin{matrix}I\\I\end{matrix}\right\} = \left(Ba''\left\{\begin{matrix}I\\I\end{matrix}\right.\right) + \left(\left.\begin{matrix}S^4O^{4''}\\Ba''\end{matrix}\right\}O^2\right)$$

Hyposulphite of barium. Iodine. Iodide of barium. Tetrathionate of barium.

**Pentathionic Acid** $\left(\left.\begin{matrix}S^5O^{4''}\\H^2\end{matrix}\right\}O^2\right)$.—If a mixture of sulphurous anhydride and hydrosulphuric acid be transmitted through water, sulphur is deposited, and the liquid assumes a milky appearance, which it loses when shaken with copper filings. If, when cold, it be saturated by carbonate of barium and filtered, it will contain pentathionate of barium, from which pentathionic acid may be prepared in the same manner as the preceding acids, by means of sulphuric acid.

The formation of pentathionic acid in this reaction is explained by the following equation:

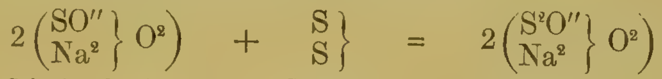


$$3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}S\right) + 4\left(SO^2\right) = \left(S^5O^{4''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right) + 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + \left.\begin{matrix}S\\S\end{matrix}\right\}$$

Hydrosulphuric acid. Sulphurous anhydride. Pentathionic acid. Water. Sulphur.

**Hyposulphites.**—Besides the preceding acids, there exists a class of salts known by the name of hyposulphites, answering to the general formula ($S^2M'^2O^3$);* the acid ($S^2H^2O^3$) and the anhydride $S^2O^2$ corresponding to these salts are unknown. If this anhydride existed, and pentathionic anhydride ($S^5O^5$) also existed, these two bodies would be polymeric.

Hyposulphite of sodium is prepared by boiling sulphur with neutral sulphite of sodium, filtering and crystallizing.



$$2\left(\left.\begin{matrix}SO''\\Na^2\end{matrix}\right\}O^2\right) + \left.\begin{matrix}S\\S\end{matrix}\right\} = 2\left(\left.\begin{matrix}S^2O''\\Na^2\end{matrix}\right\}O^2\right)$$

Sulphite of sodium. Sulphur. Hyposulphite of sodium.

Hyposulphite of sodium is much employed in the arts. Photographers utilize the property its aqueous solution possesses of dissolving the salts of silver which are insoluble in water. It is also used in dissecting rooms as an antiseptic.

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## SELENIUM $\left.\begin{matrix}Se\\Se\end{matrix}\right\}$

Atomic weight = 79·50. Molecular weight = 159.

Selenium is extracted from certain metallic selenides. These selenides are calcined with nitrate of potassium, which is a strong oxidant and causes the selenium to pass to the state of seleniate of potassium; the solution of this salt is then boiled with hydrochloric acid; free selenic acid is first produced, and afterwards it passes to the state of selenious acid.

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* The true formula of the hyposulphites is $S_2M'_2H_2O_4$; the acid would then probably be $S_2H_4O_4$, and the anhydride $S_2H_2O_3$.—(TRANS.)

$$\text{1st.}\quad \underset{\text{Seleniate of potassium.}}{\Big(\begin{matrix}SeO^{2\prime\prime}\\K^2\end{matrix}\Big\}O^2\Big)} + \underset{\text{Hydrochloric acid.}}{2\Big(\begin{matrix}H\\Cl\end{matrix}\Big\}\Big)} = \underset{\text{Chloride of potassium.}}{2\Big(\begin{matrix}K\\Cl\end{matrix}\Big\}\Big)} + \underset{\text{Selenic acid.}}{\Big(\begin{matrix}SeO^{2\prime\prime}\\H^2\end{matrix}\Big\}O^2\Big)}$$

$$\text{2nd.}\quad \underset{\text{Selenic acid.}}{\Big(\begin{matrix}SeO^{2\prime\prime}\\H^2\end{matrix}\Big\}O^2\Big)} + \underset{\text{Hydrochloric acid.}}{2\Big(\begin{matrix}H\\Cl\end{matrix}\Big\}\Big)} = \underset{\text{Chlorine.}}{\begin{matrix}Cl\\Cl\end{matrix}\Big\}} + \underset{\text{Water.}}{\Big(\begin{matrix}H\\H\end{matrix}\Big\}O\Big)} + \underset{\text{Selenious acid.}}{\Big(\begin{matrix}SeO^{\prime\prime}\\H^2\end{matrix}\Big\}O^2\Big)}$$

Finally, a current of sulphurous anhydride is transmitted through the solution of this acid. The sulphurous anhydride takes the oxygen of the selenious acid, and the selenium set free is precipitated in the form of a red powder, which is collected and agglomerated by fusion.

$$\underset{\text{Selenious acid.}}{2\Big(\begin{matrix}SeO^{\prime\prime}\\H^2\end{matrix}\Big\}O^2\Big)} + \underset{\text{Sulphurous anhydride.}}{4\big(SO^2\big)} + \underset{\text{Water.}}{2\Big(\begin{matrix}H\\H\end{matrix}\Big\}O\Big)} = \underset{\text{Sulphuric acid.}}{4\Big(\begin{matrix}SO^{2\prime\prime}\\H^2\end{matrix}\Big\}O^2\Big)} + \underset{\text{Selenium.}}{\begin{matrix}Se\\Se\end{matrix}\Big\}}$$

The selenium, melted and cooled, forms a brittle solid; it has a glassy fracture, its density is 4·8; if heated to 97° its temperature rises higher spontaneously. In one experiment, the thermometer has been known to rise to 230°; while this quantity of heat becomes disengaged the metalloid changes its appearance; it acquires a granulated fracture analogous to that of iron, and can be flattened by the hammer, of which it retains the impression, and it acquires the property of conducting heat better than when in its vitreous state. Vitreous selenium therefore bears the same relation to that which has lost caloric, as soft sulphur does to hard sulphur. M. Regnault, to whom we owe the knowledge of these facts, has recognised that precipitated selenium is in a state of vitreous modification; in fact that, like sulphur, selenium presents two allotropic states. M. Deville states that when steeped in benzine it becomes insoluble in that liquid, in which previously it was soluble.

Selenium has the same affinities as sulphur, but they are a little weaker; it burns in air, forming selenious anhydride.

## COMBINATIONS OF SELENIUM WITH BODIES PREVIOUSLY STUDIED.

### Combination with Hydrogen.

**Hydroselenic Acid** $\Big(\begin{matrix}H\\H\end{matrix}\Big\}Se\Big)$.—Hydroselenic acid is gaseous; it is obtained by treating a metallic selenide by hydrochloric acid. Its properties are analogous to those of hydrosulphuric acid. Its odour is most offensive, and resembles that of rotten cabbages.

### COMBINATIONS OF SELENIUM WITH OXYGEN.

There are two known oxygen compounds of selenium: selenious acid $\left(\left.\begin{matrix}\mathrm{SeO}'' \\ \mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right)$, and selenic acid $\left(\left.\begin{matrix}\mathrm{SeO}^{2''} \\ \mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right)$.

The anhydride ($SeO^2$) corresponding to the first of these acids is known; but the anhydride ($SeO^3$), which would correspond to the second, has not as yet been obtained.

### COMBINATIONS OF SELENIUM WITH SULPHUR.

Sulphur with selenium forms the compounds ($SeS^2$) and ($SeS^3$), corresponding to the selenious and selenic anhydrides. The first of these bodies is obtained by precipitating selenious acid by hydrosulphuric acid; and the second, by the direct combination of sulphur with selenium.

## TELLURIUM $\left.\begin{matrix}\mathrm{Te} \\ \mathrm{Te}\end{matrix}\right\}$

Atomic weight = 129. Molecular weight = 258.

To prepare tellurium, telluride of bismuth is calcined with carbonate of potassium and then treated with water. This liquid dissolves the telluride of potassium which was formed; and the solution, exposed to air, soon decomposes, liberating tellurium.

Tellurium resembles metals in its physical properties, in its lustre, its aspect, and its density, which is 6·26; its affinities are of the same nature as those of sulphur and selenium.

Tellurium forms with hydrogen a compound $\left(\left.\begin{matrix}\mathrm{H} \\ \mathrm{H}\end{matrix}\right\}\mathrm{Te}\right)$ which has received the name of hydrotelluric acid, and which is gaseous. This compound, whose properties are analogous to those of hydrosulphuric and hydroselenic acids, is obtained by treating a telluride by hydrochloric acid.

With oxygen tellurium forms two compounds; tellurous acid $\left(\left.\begin{matrix}\mathrm{TeO}'' \\ \mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right)$ and telluric acid $\left(\left.\begin{matrix}\mathrm{TeO}^{2''} \\ \mathrm{H}^{2''}\end{matrix}\right\}\mathrm{O}^2\right)$, whose anhydrides ($TeO^2$) and ($TeO^3$) are known.

Tellurium combines likewise with sulphur, and forms two sulphides, ($TeS^2$) and ($TeS^3$), which are obtained by precipitating tellurous or telluric acids by sulphuretted hydrogen; finally, tellurium forms with selenium a compound which is not well defined.*

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* The sulphide of tellurium is isomorphous with the sulphide of antimony, and telluric acid forms neither alums nor salts with biatomic metals containing seven molecules of water. These characters tend to remove tellurium from the sulphur group, and make it approach the antimony group.

## GENERAL REMARKS ON THE BIATOMIC METALLOIDS.

Oxygen, sulphur, selenium, and tellurium, being biatomic, may combine with all the monatomic metalloids, giving compounds which correspond to the general formula $R''X'^2$, in which $R''$ represents one of these four metalloids and $X'$ any monatomic radicle.

Further, we know that polyatomic radicles can accumulate indefinitely in molecules without ever being completely saturated. Generally, several polyatomic atoms form a group, the atomicity of which is equal to the sum of the capacities of saturation of each atom, diminished twice as many times as there are atoms united, less one. Thus a group of five triatomic atoms would have an atomicity equal to $(5 \times 3)-(4 \times 2) = 7$.

One consequence of this law is that the biatomic radicles, on accumulating in the molecules, form groups of which the capacity for saturation is always equal to 2. Really, $R''^2$ would have for atomicity $2 \times 2 - 2 = 2$, $R''^3$, $(2 \times 3)-(2 \times 2) = 2$, etc.

Therefore two monatomic atoms ought to be able to unite, not only to one, but to two, three, four, or *n* biatomic atoms. The limit of accumulation of these latter rests only in the stability of the compounds, and depends on the respective affinities of the elements which combine.

Thus, theoretically, all the compounds comprised in the following table are possible.

### COMPOUNDS OF OXYGEN.

| | | | | | |
|---|---|---|---|---|---|
| $H^2O$ | $Cl^2O$ | $Br^2O$ | $I^2O$ | $Fl^2O$ | $X'^2O$ |
| $H^2O^2$ | $Cl^2O^2$ | $Br^2O^2$ | $I^2O^2$ | $Fl^2O^2$ | $X'^2O^2$ |
| $H^2O^3$ | $Cl^2O^3$ | $Br^2O^3$ | $I^2O^3$ | $Fl^2O^3$ | $X'^2O^3$ |
| $H^2O^4$ | $Cl^2O^4$ | $Br^2O^4$ | $I^2O^4$ | $Fl^2O^4$ | $X'^2O^4$ |
| $H^2O^5$ | $Cl^2O^5$ | $Br^2O^5$ | $I^2O^5$ | $Fl^2O^5$ | $X'^2O^5$ |
| $H^2O^6$ | $Cl^2O^6$ | $Br^2O^6$ | $I^2O^6$ | $Fl^2O^6$ | $X'^2O^6$ |
| $H^2O^7$ | $Cl^2O^7$ | $Br^2O^7$ | $I^2O^7$ | $Fl^2O^7$ | $X'^2O^7$ |
| .. .. | .. .. | .. .. | .. .. | .. .. | .. .. |
| .. .. | .. .. | .. .. | .. .. | .. .. | .. .. |
| $H^2O^n$ | $Cl^2O^n$ | $Br^2O^n$ | $I^2O^n$ | $Fl^2O^n$ | $X'^2O^n$ |

### COMPOUNDS OF SULPHUR.

| | | | | | |
|---|---|---|---|---|---|
| $H^2S$ | $Cl^2S$ | $Br^2S$ | $I^2S$ | $Fl^2S$ | $X'^2S$ |
| $H^2S^2$ | $Cl^2S^2$ | $Br^2S^2$ | $I^2S^2$ | $Fl^2S^2$ | $X'^2S^2$ |
| $H^2S^3$ | $Cl^2S^3$ | $Br^2S^3$ | $I^2S^3$ | $Fl^2S^3$ | $X'^2S^3$ |
| $H^2S^4$ | $Cl^2S^4$ | $Br^2S^4$ | $I^2S^4$ | $Fl^2S^4$ | $X'^2S^4$ |
| $H^2S^5$ | $Cl^2S^5$ | $Br^2S^5$ | $I^2S^5$ | $Fl^2S^5$ | $X'^2S^5$ |
| $H^2S^6$ | $Cl^2S^6$ | $Br^2S^6$ | $I^2S^6$ | $Fl^2S^6$ | $X'^2S^6$ |

| | | | | | |
|---|---|---|---|---|---|
| $H^2S^7$ | $Cl^2S^7$ | $Br^2S^7$ | $I^2S^7$ | $Fl^2S^7$ | $X'^2S^7$ |
| .. .. | .. .. | .. .. | .. .. | .. .. | .. .. |
| .. .. | .. .. | .. .. | .. .. | .. .. | .. .. |
| $H^2S^n$ | $Cl^2S^n$ | $Br^2S^n$ | $I^2S^n$ | $Fl^2S^n$ | $X'^2S^n$ |

## Compounds of Selenium.

| | | | | | |
|---|---|---|---|---|---|
| $H^2Se$ | $Cl^2Se$ | $Br^2Se$ | $I^2Se$ | $Fl^2Se$ | $X'^2Se$ |
| $H^2Se^2$ | $Cl^2Se^2$ | $Br^2Se^2$ | $I^2Se^2$ | $Fl^2Se^2$ | $X'^2Se^2$ |
| $H^2Se^3$ | $Cl^2Se^3$ | $Br^2Se^3$ | $I^2Se^3$ | $Fl^2Se^3$ | $X'^2Se^3$ |
| $H^2Se^4$ | $Cl^2Se^4$ | $Br^2Se^4$ | $I^2Se^4$ | $Fl^2Se^4$ | $X'^2Se^4$ |
| $H^2Se^5$ | $Cl^2Se^5$ | $Br^2Se^5$ | $I^2Se^5$ | $Fl^2Se^5$ | $X'^2Se^5$ |
| $H^2Se^6$ | $Cl^2Se^6$ | $Br^2Se^6$ | $I^2Se^6$ | $Fl^2Se^6$ | $X'^2Se^6$ |
| $H^2Se^7$ | $Cl^2Se^7$ | $Br^2Se^7$ | $I^2Se^7$ | $Fl^2Se^7$ | $X'^2Se^7$ |
| .. .. | .. .. | .. .. | .. .. | .. .. | .. .. |
| .. .. | .. .. | .. .. | .. .. | .. .. | .. .. |
| $H^2Se^n$ | $Cl^2Se^n$ | $Br^2Se^n$ | $I^2Se^n$ | $Fl^2Se^n$ | $X'^2Se^n$ |

## Compounds of Tellurium.

| | | | | | |
|---|---|---|---|---|---|
| $H^2Te$ | $Cl^2Te$ | $Br^2Te$ | $I^2Te$ | $Fl^2Te$ | $X'^2Te$ |
| $H^2Te^2$ | $Cl^2Te^2$ | $Br^2Te^2$ | $I^2Te^2$ | $Fl^2Te^2$ | $X'^2Te^2$ |
| $H^2Te^3$ | $Cl^2Te^3$ | $Br^2Te^3$ | $I^2Te^3$ | $Fl^2Te^3$ | $X'^2Te^3$ |
| $H^2Te^4$ | $Cl^2Te^4$ | $Br^2Te^4$ | $I^2Te^4$ | $Fl^2Te^4$ | $X'^2Te^4$ |
| $H^2Te^5$ | $Cl^2Te^5$ | $Br^2Te^5$ | $I^2Te^5$ | $Fl^2Te^5$ | $X'^2Te^5$ |
| $H^2Te^6$ | $Cl^2Te^6$ | $Br^2Te^6$ | $I^2Te^6$ | $Fl^2Te^6$ | $X'^2Te^6$ |
| $H^2Te^7$ | $Cl^2Te^7$ | $Br^2Te^7$ | $I^2Te^7$ | $Fl^2Te^7$ | $X'^2Te^7$ |
| .. .. | .. .. | .. .. | .. .. | .. .. | .. .. |
| .. .. | .. .. | .. .. | .. .. | .. .. | .. .. |
| $H^2Te^n$ | $Cl^2Te^n$ | $Br^2Te^n$ | $I^2Te^n$ | $Fl^2Te^n$ | $X'^2Te^n$ |

As a fact, all these compounds do not exist. Is it because the affinity of oxygen and its congeners for hydrogen, bromine, iodine, and fluorine, is too weak to allow of such an accumulation of polyatomic radicles in one molecule, or is it possible that these bodies exist, though not yet discovered? Both hypotheses may be held, on condition that too great a value be not attributed to *n*. However it may be, those compounds that are known are the following—

## Oxygen Compounds.

Water ($H^2O$)
Hypochlorous anhydride ($Cl^2O$).
Hypobromous anhydride ($Br^2O$).
Oxygenized water ($H^2O^2$)
Probable binoxide of chlorine ($Cl^2O^2$).
Chlorous anhydride ($Cl^2O^3$).
Hypochloride ($ClO^2$).
Iodic anhydride ($I^2O^5$).

To which must be added chloric anhydride ($Cl^2O^5$), bromic anhydride ($Br^2O^5$), perchloric anhydride ($Cl^2O^7$), perbromic anhydride ($Br^2O^7$), and periodic anhydride ($I^2O^7$): compounds that are still unknown, but whose corresponding acids are known.

### SULPHUR COMPOUNDS.

Hydrosulphuric acid ($H^2S$).
Bisulphide of hydrogen ($H^2S^2$).

Bichloride of sulphur ($Cl^2S$).
Protochloride of sulphur ($Cl^2S^2$).

### COMPOUNDS OF SELENIUM.

Hydroselenic acid ($H^2Se$).

Chloride of selenium ($Cl^2Se$).

### TELLURIC COMPOUNDS.

Hydrotelluric acid ($H^2Te$).
Chloride of tellurium ($Cl^2Te$).

Bromide of tellurium ($Br^2Te$).
Iodide of tellurium ($I^2Te$).

There are also compounds of sulphur and selenium with bromine and iodine, but they are not well known.

We have hitherto supposed oxygen, sulphur, selenium, and tellurium to be biatomic; and this manner of considering these bodies is allowable, because they act as bivalents in most cases. There are, nevertheless, some rare compounds in which they are tetravalent. These are the three chlorides ($SCl^4$), ($SeCl^4$), ($TeCl^4$), and the sub-oxide of silver ($Ag^4O$), etc.

Biatomic metalloids may also combine among themselves. We will not dwell on these compounds which theory enables us to foresee, the number is naturally unlimited. Sulphur, selenium, and tellurium form part of oxy-acids the anhydrides of which are sulphurous anhydride ($SO^2$), selenious anhydride ($SeO^2$), tellurous anhydride ($TeO^2$), sulphuric anhydride ($SO^3$), selenic anhydride (unknown) ($SeO^3$), telluric anhydride ($TeO^3$).

There also exists a certain number of acids of sulphur whose anhydrides are unknown, and whose corresponding selenium and tellurium compounds have not yet been discovered. These are—

1st. Hyposulphurous acid .. $\left(S^2O''\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)$, or, rather, metallic hyposulphites, for the acid itself is not stable.

2nd. Dithionic acid .. .. $\left(S^2O^{4''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)$

3rd. Trithionic acid .. .. $\left(S^3O^{4''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)$

4th. Tetrathionic acid .. $\left(S^4O^{4''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)$

5th. Pentathionic acid .. $\left(S^5O^{4''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)$

If ever the means of preparing hyposulphurous and pentathionic anhydrides be discovered these bodies will be polymeric. The hyposulphurous anhydride would have for formula ($S^2O^2$), and the pentathionic anhydride ($S^5O^5$).

We have already seen that selenium and tellurium may also combine with sulphur, forming compounds which correspond to the oxygenized combinations of these bodies.

## THIRD GROUP (TRIATOMIC METALLOIDS).

### BORON $\left.\begin{matrix}B'''\\B'''\end{matrix}\right\}$ ?

Atomic weight = 11. Molecular weight unknown.

Boron can be obtained by three different processes, each of which gives it with different properties.

1st. Boracic anhydride is decomposed at red heat by sodium, and the mass is poured into water acidulated with hydrochloric acid.

$$\underset{\text{Boracic anhydride.}}{2\left(B^2O^3\right)} + \underset{\text{Sodium.}}{3\left(\left.\begin{matrix}Na\\Na\end{matrix}\right\}\right)} = \underset{\text{Borate of sodium.}}{2\left(\left.\begin{matrix}B''\\Na^3\end{matrix}\right\}O^3\right)} + \underset{\text{Boron.}}{\left.\begin{matrix}B'''\\B'''\end{matrix}\right\}}$$

The boron thus obtained is amorphous, and brownish in colour.

2nd. A current of chloride of boron is transmitted on to melted aluminium. Chloride of aluminium is produced, which is volatilized, and the boron is dissolved in the excess of aluminium.

$$\underset{\text{Aluminium.}}{2\left(Al\right)} + \underset{\text{Chloride of boron.}}{2\left(B'''Cl^3\right)} = \underset{\text{Chloride of aluminium.}}{\left(\left.\begin{matrix}Al^2\\Cl^6\end{matrix}\right\}\right)} + \underset{\text{Boron.}}{\left.\begin{matrix}B'''\\B'''\end{matrix}\right\}}$$

After a time the continued volatilization of the aluminium and the continuous addition of boron cause the super-saturation of the solvent, and the boron is deposited in hexagonal prismatic crystals, which are opaque, and of a brown colour. These are purified by boiling with hydrochloric acid, which dissolves the aluminium. This boron has been called graphitoid, from certain analogies which have been observed between it and graphite.* (*See* Carbon).

3rd. Boracic anhydride is calcined with aluminium, and oxide of aluminium and boron are formed.

$$\underset{\text{Aluminium.}}{2\left(Al\right)} + \underset{\text{Boracic anhydride.}}{\left(B^2O^3\right)} = \underset{\text{Oxide of aluminium.}}{\left(Al^2O^3\right)} + \underset{\text{Boron.}}{\left.\begin{matrix}B'''\\B'''\end{matrix}\right\}}$$

To purify the boron thus prepared, it is first boiled with a solution of hydrate of potassium, then with hydrochloric acid, and, finally, it is mechanically separated from the oxide of aluminium with which it is mixed.

Boron is then transparent, rather yellow, crystallized in prisms with a square base, nearly as hard and as refracting as the diamond; its density is 2·68. M. Deville has called it the boron diamond. Boron will not melt at any temperature; it becomes oxidized at the same temperature which causes the combustion of the diamond, and is then transformed into boracic anhydride. At red heat it burns in gaseous chlorine, forming chloride of boron.

---

* Wœhler and Deville have recently shown this to be a compound ($AlB^2$).—Trans.

Acids do not affect it, unless it be aqua regia, which seems after a length of time to dissolve it sparingly.

Potash and soda act upon it at red heat.

Bisulphate of potassium transforms it into boracic anhydride, disengaging sulphurous anhydride and water.

$$\underset{\text{Bisulphate of potassium.}}{6\left(\left.\begin{matrix}SO^{2\prime\prime}\\ KH\end{matrix}\right\}O^2\right)} + \underset{\text{Boron.}}{\left.\begin{matrix}B'''\\ B'''\end{matrix}\right\}} =$$

$$\underset{\text{Boracic anhydride.}}{\left(B^2O^3\right)} + \underset{\text{Neutral sulphate of potassium.}}{3\left(\left.\begin{matrix}SO^{2\prime\prime}\\ K^2\end{matrix}\right\}O^2\right)} + \underset{\text{Water.}}{3\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)} + \underset{\text{Sulphurous anhydride.}}{3\left(SO^2\right)}$$

Boron when heated combines directly with the nitrogen of the air, forming a nitride.

Amorphous boron, when it has not been too strongly calcined, enters into combination a little more readily than the two other varieties of this body.

Do these three varieties of boron constitute three different allotropic states, or do they belong to the domain of polymorphism? This will be difficult to decide until new experiments have elucidated the question.

### COMBINATIONS OF BORON WITH MONATOMIC METALLOIDS.

Boron combines with these metalloids, giving compounds which correspond to the general formula $BX^3$. The chloride, bromide, and fluoride of boron only are known as yet, but it is probable that the iodide of boron, and perhaps even boretted hydrogen may be obtained.

**Chloride and Bromide of Boron.**—Chloride of boron is prepared by passing a current of chlorine over a mixture of boracic anhydride and carbon heated to redness; the carbon takes the oxygen, while the boron combines with the chlorine.

$$\underset{\text{Boracic anhydride.}}{\left(B^2O^3\right)} + \underset{\text{Carbon.}}{3\left(C\right)} + \underset{\text{Chlorine.}}{6\left(\left.\begin{matrix}Cl\\ Cl\end{matrix}\right\}\right)} = \underset{\text{Oxide of carbon.}}{3\left(CO\right)} + \underset{\text{Chloride of boron.}}{2\left(B'''\left\{\begin{matrix}Cl\\ Cl\\ Cl\end{matrix}\right.\right)}$$

The mixture of boracic anhydride and carbon is made by mixing the two bodies finely powdered, and making them into a paste with starch. When the paste is firm enough it is rolled into balls, and these are calcined in a crucible; the starch is destroyed, and we have thus small balls formed of boracic anhydride and carbon.

These balls are placed in a tubulated stoneware retort in a reverberatory furnace (fig. 26); into the upper part of this retort there passes a porcelain tube, which goes to the bottom. This tube is sufficiently long to prevent its getting very hot at its upper part, so that by means of a glass tube and a cork it may be placed in communication with the apparatus in which the chlorine is produced.

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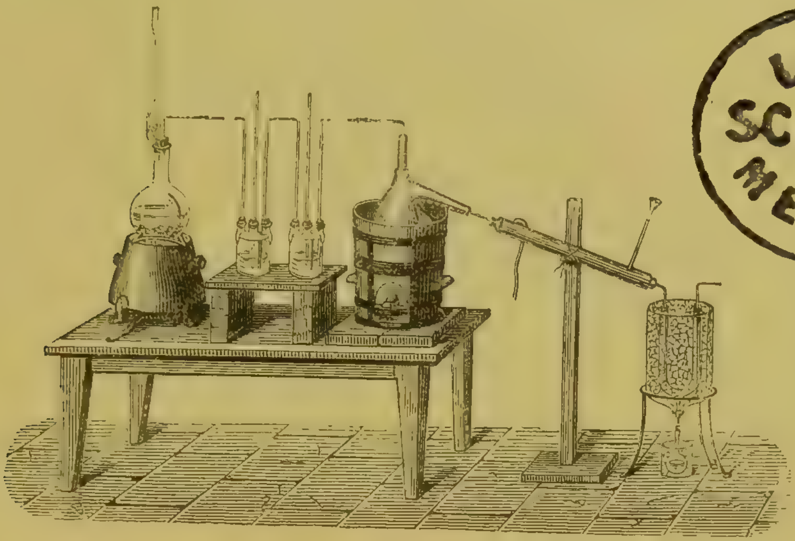

Fig. 26.

The lateral tube of the retort is joined to the refrigerating apparatus intended to condense the product.

When the apparatus is thus prepared, on making the retort containing the mixture of boracic anhydride and carbon red hot, and directing into it a current of very dry chlorine, chloride of boron is produced.

Under the influence of water, chloride of boron decomposes into hydrochloric and boracic acids.

$$\underset{\text{Chloride of boron.}}{\left(BCl^3\right)} + \underset{\text{Water.}}{3\left(\begin{matrix}H\\H\end{matrix}\right\}O\Big)} = \underset{\text{Hydrochloric acid.}}{3\left(\begin{matrix}H\\Cl\end{matrix}\right\}\Big)} + \underset{\text{Boracic acid.}}{\left(\begin{matrix}B'''\\H^3\end{matrix}\right\}O^3\Big)}$$

The bromide of boron would probably be obtained by a similar process, but as yet it has only been prepared by the direct action of bromine vapour on red-hot boron.

**Fluoride of Boron.**—The fluoride of boron is obtained by heating boracic anhydride with fluoride of calcium to bright redness.

$$\underset{\text{Boracic anhydride.}}{2\left(B^2O^3\right)} + \underset{\text{Fluoride of calcium.}}{3\left(CaFl^2\right)} = \underset{\text{Fluoride of boron.}}{2\left(BFl^3\right)} + \underset{\text{Borate of calcium.}}{\left(\begin{matrix}B'''^2\\Ca^3\end{matrix}\right\}O^6\Big)}$$

Fluoride of boron may also be prepared by heating a mixture of fluoride of calcium, sulphuric acid, and boracic anhydride:

$$\underset{\substack{\text{Boracic}\\\text{anhydride.}}}{\left(B^2O^3\right)} + \underset{\substack{\text{Fluoride of}\\\text{calcium.}}}{3\left(CaFl^2\right)} + \underset{\text{Sulphuric acid.}}{3\left(\left.\begin{matrix}SO^{2\prime\prime}\\H^2\end{matrix}\right\}O^2\right)} = \underset{\substack{\text{Sulphate of}\\\text{calcium.}}}{3\left(\left.\begin{matrix}SO^{2\prime\prime}\\Ca^{\prime\prime}\end{matrix}\right\}O^2\right)} + \underset{\text{Water.}}{3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\substack{\text{Fluoride of}\\\text{boron.}}}{2\left(BFl^3\right)}$$

Fluoride of boron on contact with water gives rise to acids, which are called borofluoric and hydrofluoboric, whose constitution is not well known. The latter, nevertheless, seems to be the result of the union of a molecule of hydrofluoric acid with a molecule of fluoride of boron. It enters into double decomposition with bases, and produces double fluorides of boron and the metal of the base.

If this be really its composition, its mode of formation and its action on bases would be expressed by the following formulas:

$$\underset{\substack{\text{Fluoride of}\\\text{boron.}}}{4\left(BFl^3\right)} + \underset{\text{Water.}}{3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Hydrofluoboric acid.}}{3\left(BFl^3,HFl\right)} + \underset{\substack{\text{Boracic}\\\text{acid.}}}{\left(\left.\begin{matrix}B^{\prime\prime\prime}\\H^3\end{matrix}\right\}O^3\right)}$$

$$\underset{\text{Hydrofluoboric acid.}}{\left(BFl^3,HFl\right)} + \underset{\substack{\text{Hydrate of}\\\text{potassium.}}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\substack{\text{Double fluoride of}\\\text{boron and potassium.}}}{\left(BFl^3,KFl\right)}$$

## Combinations of Boron with Biatomic Metalloids.

Combinations of boron with sulphur and oxygen are known. They have for formula $(B^2O^3)$ and $(B^2S^3)$.

The first of these bodies is an anhydride, which, on reacting with water, is transformed into triatomic boracic acid.

$$\underset{\substack{\text{Boracic}\\\text{anhydride.}}}{\left(B^2O^3\right)} + \underset{\text{Water.}}{3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Boracic acid.}}{2\left(\left.\begin{matrix}B^{\prime\prime\prime}\\H^3\end{matrix}\right\}O^3\right)}$$

The second, on contact with water, decomposes, giving rise to boracic and hydrosulphuric acids.

$$\underset{\substack{\text{Sulphide}\\\text{of boron.}}}{\left(B^2S^3\right)} + \underset{\text{Water.}}{6\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\substack{\text{Hydrosulphuric}\\\text{acid.}}}{3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}S\right)} + \underset{\text{Boracic acid.}}{2\left(\left.\begin{matrix}B^{\prime\prime\prime}\\H^3\end{matrix}\right\}O^3\right)}$$

Boracic acid is procured from the gaseous exhalations (called *soffioni*) of the soil in Tuscany on the borders of small lakes, whose waters yield it on simple evaporation. This water always containing hydrosulphuric acid, we must suppose that the soil of Tuscany contains at a great depth sulphide of boron, and that this sulphide is decomposed by the vapour of water, of which the soffioni are chiefly composed.

Boracic acid at 100° loses a molecule of water, forming a first anhydride $\left(\left.\begin{matrix}\mathrm{BO}'\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)$. At red heat this anhydride is doubled, while it loses at the same time a second molecule of water to form a second boracic anhydride.

$$\underset{\text{1st boracic anhydride.}}{\left(\left.\begin{matrix}\mathrm{BO}'\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}+\underset{\text{1st boracic anhydride.}}{\left(\left.\begin{matrix}\mathrm{BO}'\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}=\underset{\text{Ordinary boracic anhydride.}}{\left(\left.\begin{matrix}\mathrm{B}'''\\ \mathrm{B}'''\end{matrix}\right\}\mathrm{O}^3\right)}+\underset{\text{Water.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}$$

This phenomenon is often met with in chemistry. The acids containing more than two atoms of typical hydrogen, after losing a molecule of water, still contain typical hydrogen. The result is that these acids may give rise to several anhydrides presenting different degrees of dehydration. The number of anhydrides possible, is equal to the number of atoms of typical hydrogen which the acid contains. The same phenomenon is also observed with polyatomic bases.

### COMBINATIONS OF BORON WITH TETRA AND PENTATOMIC METALLOIDS.

No definite combination of boron with tetratomic metalloids is known. Among the pentatomic metalloids there is one, nitrogen, which combines with boron. The formula of nitride of boron is $(\mathrm{B}'''\mathrm{N})$; bases decompose it into ammonia and metallic borate.

$$\underset{\text{Nitride of boron.}}{\left(\mathrm{BN}\right)}+\underset{\text{Hydrate of potassium.}}{3\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}=\underset{\text{Borate of potassium.}}{\left(\left.\begin{matrix}\mathrm{B}'''\\ \mathrm{K}^3\end{matrix}\right\}\mathrm{O}^3\right)}+\underset{\text{Ammonia.}}{\mathrm{NH}^3}$$

## FOURTH GROUP (TETRATOMIC METALLOIDS).

### SILICON $\mathrm{Si}^{\mathrm{iv}}$.

Atomic weight = 28. Molecular weight unknown.

Silicon may be obtained in several ways, and possesses properties which differ according to the method used for its preparation.

1st. The double fluoride of silicon and potassium is calcined with potassium. Silicon and fluoride of potassium are formed, and are to be treated with water, which dissolves the latter salt and leaves the silicon free.

Thus prepared, silicon is brown, amorphous, infusible, and insoluble in all menstrua. At a high temperature it becomes oxidized, but always incompletely, because the oxide formed preserves the silicon not yet acted on. Calcined with hydrate of potassium, this body gives rise to silicate of potassium, and hydrogen is disengaged.

$$\underset{\text{Silicon.}}{\mathrm{Si}^{\mathrm{iv}}}+\underset{\text{Hydrate of potassium.}}{4\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}=\underset{\text{Silicate of potassium.}}{\left(\left.\begin{matrix}\mathrm{Si}^{\mathrm{iv}}\\ \mathrm{K}^4\end{matrix}\right\}\mathrm{O}^4\right)}+\underset{\text{Hydrogen.}}{2\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\right)}$$

2nd. Silicon may be prepared by transmitting its chloride over melted aluminium, as was the case with boron. By this method brilliant scales are obtained, which differ from the preceding silicon by their external properties. M. Deville has named this graphitoidal silicon.

3rd. The vapour of chloride of silicon may be decomposed by melted sodium: the silicon thus obtained is amorphous, but when heated with sea salt at a very high temperature it melts and then crystallizes. Its crystals assume the same form as the diamond, are able to cut glass, and no longer present any properties of ordinary silicon. It is known as crystalline silicon.

Do amorphous, graphitoidal, and crystalline silicon constitute three allotropic states of one body, or do these three modifications proceed from polymorphism? At present this has not been decided.

## COMBINATIONS OF SILICON WITH METALLOIDS PREVIOUSLY STUDIED.

**Chloride of Silicon** $\left(\left.\begin{matrix}Si^{iv}\\Cl^4\end{matrix}\right\}\right)$.—This body is obtained by passing a current of dry chlorine over a mixture of silicic anhydride and carbon, heated to redness.

$$\underset{\text{Silicic anhydride.}}{(SiO^2)} + \underset{\text{Carbon.}}{C} + \underset{\text{Chlorine.}}{2\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}\right)} = \underset{\text{Carbonic anhydride.}}{(CO^2)} + \underset{\text{Chloride of silicon.}}{(SiCl^4)}$$

The same method is employed as that used for the preparation of chloride of boron.

Chloride of silicon is liquid: on contact with water it decomposes into hydrochloric and silicic acids.

$$\underset{\text{Chloride of silicon.}}{(SiCl^4)} + \underset{\text{Water.}}{4\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Silicic acid.}}{\left(\left.\begin{matrix}Si^{iv}\\H^4\end{matrix}\right\}O^4\right)} + \underset{\text{Hydrochloric acid.}}{4\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)}$$

On heating silicon nearly to redness in a current of dry hydrochloric acid gas, a product is obtained which seems to have for formula $(Si^3Cl^6,4HCl)$? (old notation $[Si^2Cl^3,2HCl]$).

**Bromide of Silicon** $\left(\left.\begin{matrix}Si^{iv}\\Br^4\end{matrix}\right\}\right)$.—This is obtained by a similar process as the chloride: it is liquid like the chloride, and decomposes in an analogous manner on contact with water into hydrobromic and silicic acids.

Silicon heated to dull redness in a current of hydrobromic acid gas gives a compound the formula of which appears to be $(Si^3Br^6,4HBr)$? (old notation $[Si^2Br^3,3HBr]$).

**Iodide of Silicon** $\left(\left.\begin{matrix}Si^{iv}\\I^4\end{matrix}\right\}\right)$. — This compound has not yet been obtained; but when gaseous hydriodic acid is made to act on silicon heated to low redness, a body is produced, the formula of which seems to be $(Si^3I^6,4HI)$? (old notation $[Si^2I^3,2HI]$).*

---

* I have said, following M. Wœhler, that silicon, when heated in a current of gaseous and dry hydrochloric, hydrobromic, or hydriodic acid, furnishes bodies answering to the formulæ—

$$[Si^3Cl^6,4HCl] \quad [Si^3Br^6,4HBr] \quad [Si^3I^6,4HI].$$

These formulæ appeared to me to be scarcely probable; so, to avoid being accused of having badly translated them from the old to the new notation, I gave the two notations side by side.

Messrs. Friedel and Ladenburg have just justified my doubts. These chemists, on rectifying Wœhler's compound, have obtained a liquid which is volatile at from 34° to 37°, answering to the formula $(SiHCl^3)$. This formula is that of chloroform $(CHCl^3)$, with the carbon replaced by silicon; and not only its formula but also its reactions lead us to regard it as silicated chloroform.

1st. Under the influence of ethylate of sodium, chloroform exchanges its three atoms of chlorine for three atoms of ox-ethyl, and furnishes the compound $\left(C\begin{cases}H\\OC^2H^5\\OC^2H^5\\OC^2H^5\end{cases}\right)$.

$$\underset{\text{Chloroform.}}{\left(C\begin{cases}H\\Cl\\Cl\\Cl\end{cases}\right)} + \underset{\text{Ethylate of sodium.}}{3(NaOC^2H^5)} = \underset{\text{Chloride of sodium.}}{3(NaCl)} + \left(C\begin{cases}H\\OC^2H^5\\OC^2H^5\\OC^2H^5\end{cases}\right)$$

Silicated chloroform gives an identical reaction when made to act on alcohol.

$$\underset{\text{Silicated chloroform.}}{\left(Si\begin{cases}H\\Cl\\Cl\\Cl\end{cases}\right)} + \underset{\text{Alcohol.}}{3(HOC^2H^5)} = \underset{\text{Hydrochloric acid.}}{3(HCl)} + \left(Si\begin{cases}H\\OC^2H^5\\OC^2H^5\\OC^2H^5\end{cases}\right)$$

2nd. Silicated chloroform, when treated by alcoholic potash, exchanges 2Cl for O, and Cl for OK, in order to give formiate of potassium, and consequently formic acid.

Treated by water it exchanges its chlorine for oxygen, and furnishes, not the acid, but formic anhydride, which contains silicon instead of carbon.

$$2\underset{\text{Silicated chloroform.}}{\left(Si\begin{cases}H\\Cl\\Cl\\Cl\end{cases}\right)} + \underset{\text{Water.}}{3(H^2O)} = \underset{\text{Hydrochloric acid.}}{6(HCl)} + \underbrace{\left(\begin{matrix}Si\begin{cases}H\\O''\end{cases}\\ \quad O''\\ Si\begin{cases}O''\\H\end{cases}\end{matrix}\right) = \left(\left.\begin{matrix}SiHO\\SiHO\end{matrix}\right\} O\right)}_{\text{Silicated formic anhydride.}}$$

When the body $\left(Si\begin{cases}H\\OC^2H^5\\OC^2H^5\\OC^2H^5\end{cases}\right)$ is submitted to the action of sodium, this metal, by virtue of a catalytic action, divides it into silicate of ethyl and silicated hydrogen. MM. Friedel and Ladenburg have obtained pure silicated hydrogen for analysis by this method, which has also enabled them to establish experimentally that its formula is indeed $(SiH^4$ , as chemists supposed. The reaction which gives rise to this gas is expressed by the following equation:—

$$4\left(Si\begin{cases}H\\OC^2H^5\\OC^2H^5\\OC^2H^5\end{cases}\right) = \underset{\text{Silicated hydrogen.}}{\left(Si\begin{cases}H\\H\\H\\H\end{cases}\right)} + 3\underset{\text{Silicate of ethyl.}}{\left(Si\begin{cases}OC^2H^5\\OC^2H^5\\OC^2H^5\\OC^2H^5\end{cases}\right)}$$

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**Fluoride of Silicon** $\left(\left.\begin{matrix}Si^{iv}\\Fl^4\end{matrix}\right\}\right)$.—This fluoride is obtained by causing hydrofluoric acid to act on silicic anhydride, or, which is the same thing, by submitting this anhydride to the action of a mixture of sulphuric acid and fluoride of calcium.

$$\begin{array}{ccccccc}\left(SiO^2\right) & + & 4\left(\left.\begin{matrix}H\\Fl\end{matrix}\right\}\right) & = & \left(\left.\begin{matrix}Si^{iv}\\Fl^4\end{matrix}\right\}\right) & + & 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)\\ \text{Silicic anhydride.} & & \text{Hydrofluoric acid.} & & \text{Fluoride of silicon.} & & \text{Water.}\end{array}$$

Fluoride of silicon is a gas which in the air emits thick white fumes. It may be liquefied by means of strong pressure and considerable cold. Water decomposes it, forming silicic acid, and another acid which has received the name of hydrofluosilicic acid, and which corresponds to the formula $(2HFl,Si^{iv}Fl^4)$.

$$\begin{array}{ccccccc}3\left(\left.\begin{matrix}Si^{iv}\\Fl^4\end{matrix}\right\}\right) & + & 4\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) & = & \left(\left.\begin{matrix}Si^{iv}\\H^4\end{matrix}\right\}O^4\right) & + & 2\left(Si^{iv}Fl^4,2HFl\right)\\ \text{Fluoride of silicon.} & & \text{Water.} & & \text{Silicic acid.} & & \text{Hydrofluosilicic acid.}\end{array}$$

Hydrofluosilicic acid undergoes double decomposition with bases, and thus gives rise to double fluorides.

$$\begin{array}{ccccccc}\left(Si^{iv}Fl^4,2HFl\right) & + & 2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right) & = & \left(Si^{iv}Fl^4,2KFl\right) & + & 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)\\ \text{Hydrofluosilicic acid.} & & \text{Hydrate of potassium.} & & \text{Double fluoride of silicon and potassium.} & & \text{Water.}\end{array}$$

**Silicated Hydrogen.**—Silicated hydrogen is formed when the silicide of magnesium is decomposed by hydrochloric acid.

$$\begin{array}{ccccccc}\left(Si^{iv}Mg^2\right) & + & 4\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right) & = & 2\left(\left.\begin{matrix}Mg''\\Cl^2\end{matrix}\right\}\right) & + & \left(\left.\begin{matrix}Si^{iv}\\H^4\end{matrix}\right\}\right)\\ \text{Silicide of magnesium.} & & \text{Hydrochloric acid.} & & \text{Chloride of magnesium.} & & \text{Silicated hydrogen.}\end{array}$$

This body has not as yet been obtained in a pure state.

**Silicic Anhydride** $(SiO^2)$. (Synonym: *Silica*).—Silica is very abundantly distributed in nature. It occurs in rock crystal, quartzose sand, agate, flint, etc. It may be obtained very pure by transmitting a current of gaseous fluoride of silicon into water, collecting on a filter the gelatinous precipitate which is deposited, and drying it by a gentle heat.

Silica is insoluble in pure water, in alkaline solutions, and in acids.

No metalloid decomposes it; but at a high temperature it may be decomposed by causing two bodies to act, the one having affinity for oxygen and the other for silicon; carbon and chlorine, for example.

Silicon forms salts when heated with bases or basic anhydrides. These salts answer generally to the formula $\left(\left.\begin{matrix}Si^{iv}\\R^4\end{matrix}\right\}O^4\right)$.

Its salts of potash or soda are soluble; hydrochloric acid, nitric acid, carbonic anhydride, etc., precipitate a gelatinous hydrate of silica, probably silicic acid $\left(\left.\begin{matrix}Si^{iv}\\H^4\end{matrix}\right\}O^4\right)$. An excess of hydrochloric acid redissolves the precipitate.

Gelatinous silicic acid loses water in the air, and is transformed into a condensed acid answering to the formula $\left(\left.\begin{matrix}Si^{\text{iv}3}\\H^{4}\end{matrix}\right\}O^{8}\right)$, which seems to be the second anhydride of an unknown acid whose formula would be $\left(\left.\begin{matrix}Si^{3}\\H^{8}\end{matrix}\right\}O^{10}\right)$.

$$\left(\left.\begin{matrix}Si^{3}\\H^{8}\end{matrix}\right\}O^{10}\right) - 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}Si^{3}\\H^{4}\end{matrix}\right\}O^{8}\right)$$

The acid $\left(\left.\begin{matrix}Si^{3}\\H^{4}\end{matrix}\right\}O^{8}\right)$, heated to 100°, loses the half of its hydrogen in the state of water and is transformed into a new anhydride $\left(\left.\begin{matrix}Si^{3}\\H^{2}\end{matrix}\right\}O^{7}\right)$.

M. Ebelmen, on decomposing silicic ether by water, has obtained a silicic acid which has for formula $\left(\left.\begin{matrix}Si^{2}\\H^{4}\end{matrix}\right\}O^{6}\right)$. This is probably the first anhydride of an unknown acid whose formula would be $\left(\left.\begin{matrix}Si^{2}\\H^{6}\end{matrix}\right\}O^{7}\right)$.

The known hydrates of silica are far from being the only possible ones: theoretically, we may admit the existence of the following hydrates:—

SATURATED ACIDS. ANHYDRIDES.

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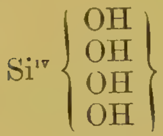
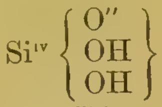


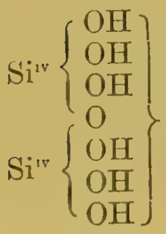
$$Si^{\text{iv}}\left\{\begin{matrix}OH\\OH\\OH\\OH\end{matrix}\right\}$$

Silicic acid.



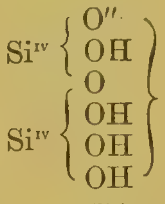
$$Si^{\text{iv}}\left\{\begin{matrix}O''\\OH\\OH\end{matrix}\right\}$$

First silicic anhydride.



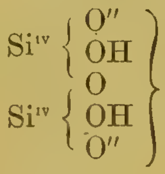
$$\left.\begin{matrix}Si^{\text{iv}}\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.\\O\\Si^{\text{iv}}\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.\end{matrix}\right\}$$

Disilicic acid.



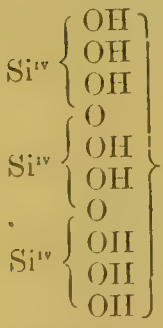
$$\left.\begin{matrix}Si^{\text{iv}}\left\{\begin{matrix}O''\\OH\end{matrix}\right.\\O\\Si^{\text{iv}}\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.\end{matrix}\right\}$$

1st Disilicic anhydride.



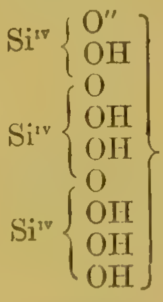
$$\left.\begin{matrix}Si^{\text{iv}}\left\{\begin{matrix}O''\\OH\end{matrix}\right.\\O\\Si^{\text{iv}}\left\{\begin{matrix}OH\\O''\end{matrix}\right.\end{matrix}\right\}$$

2nd Disilicic anhydride.



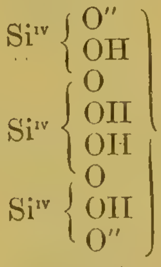
$$\left.\begin{matrix}Si^{\text{iv}}\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.\\O\\Si^{\text{iv}}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\\O\\Si^{\text{iv}}\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.\end{matrix}\right\}$$

Trisilicic acid.



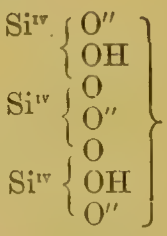
$$\left.\begin{matrix}Si^{\text{iv}}\left\{\begin{matrix}O''\\OH\end{matrix}\right.\\O\\Si^{\text{iv}}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\\O\\Si^{\text{iv}}\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.\end{matrix}\right\}$$

1st Trisilicic anhydride.



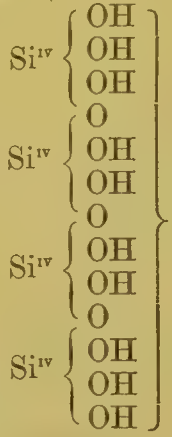
$$\left.\begin{matrix}Si^{\text{iv}}\left\{\begin{matrix}O''\\OH\end{matrix}\right.\\O\\Si^{\text{iv}}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\\O\\Si^{\text{iv}}\left\{\begin{matrix}OH\\O''\end{matrix}\right.\end{matrix}\right\}$$

2nd Trisilicic anhydride.



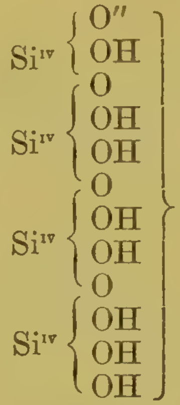
$$\left.\begin{matrix}Si^{\text{iv}}\left\{\begin{matrix}O''\\OH\end{matrix}\right.\\O\\Si^{\text{iv}}\left\{O''\right.\\O\\Si^{\text{iv}}\left\{\begin{matrix}OH\\O''\end{matrix}\right.\end{matrix}\right\}$$

3rd Trisilicic anhydride.



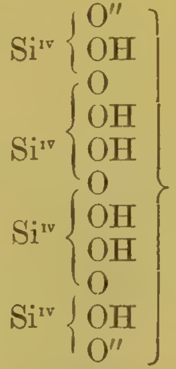
$$\left.\begin{array}{rl} & \mathrm{OH} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{OH} \end{array}\right\}$$

Tetrasilicic acid.



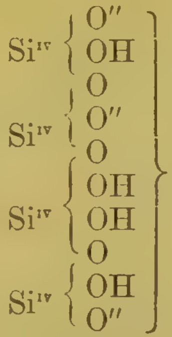
$$\left.\begin{array}{rl} & \mathrm{O}'' \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{OH} \end{array}\right\}$$

1st Tetrasilicic anhydride..



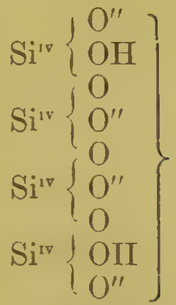
$$\left.\begin{array}{rl} & \mathrm{O}'' \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{O} \\ & \mathrm{OH} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{O}'' \end{array}\right\}$$

2nd Tetrasilicic anhydride.



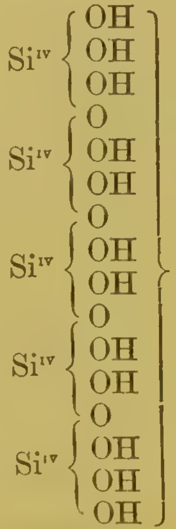
$$\left.\begin{array}{rl} & \mathrm{O}'' \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{O}'' \\ & \mathrm{O} \\ & \mathrm{OH} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{O}'' \end{array}\right\}$$

3rd Tetrasilicic anhydride.



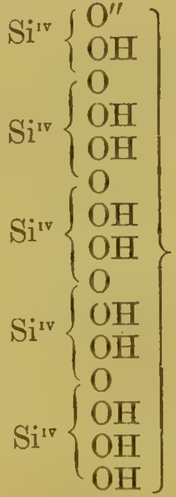
$$\left.\begin{array}{rl} & \mathrm{O}'' \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{O}'' \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{O}'' \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{O}'' \end{array}\right\}$$

4th Tetrasilicic anhydride.



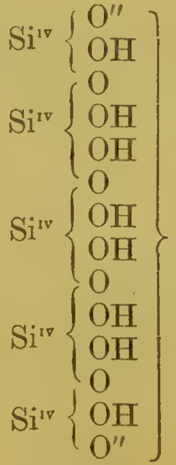
$$\left.\begin{array}{rl} & \mathrm{OH} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{OH} \end{array}\right\}$$

Pentasilicic acid.



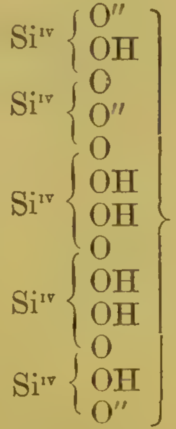
$$\left.\begin{array}{rl} & \mathrm{O}'' \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ & \mathrm{OH} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \end{array}\right\}$$

1st Pentasilicic anhydride.



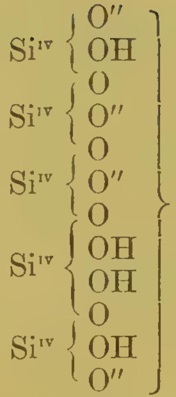
$$\left.\begin{array}{rl} & \mathrm{O}'' \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{O}'' \end{array}\right\}$$

2nd Pentasilicic anhydride.



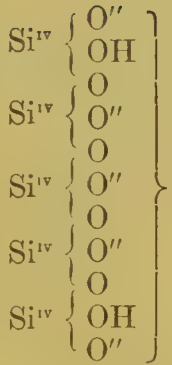
$$\left.\begin{array}{rl} & \mathrm{O}'' \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{O}'' \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{O}'' \end{array}\right\}$$

3rd Pentasilicic anhydride.



$$\left.\begin{array}{rl} & \mathrm{O}'' \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{O}'' \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{O}'' \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{O}'' \end{array}\right\}$$

4th Pentasilicic anhydride.



$$\left.\begin{array}{rl} & \mathrm{O}'' \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{O}'' \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{O}'' \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{O}'' \\ & \mathrm{O} \\ \mathrm{Si}^{\mathrm{iv}} & \mathrm{OH} \\ & \mathrm{O}'' \end{array}\right\}$$

5th Pentasilicic anhydride.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $\left.\begin{array}{ll} \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{OH} \end{array}\right\}$ | $\left.\begin{array}{ll} \mathrm{Si^{iv}} & \mathrm{O''} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{OH} \end{array}\right\}$ | $\left.\begin{array}{ll} \mathrm{Si^{iv}} & \mathrm{O''} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{O''} \end{array}\right\}$ | $\left.\begin{array}{ll} \mathrm{Si^{iv}} & \mathrm{O''} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{O''} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{O''} \end{array}\right\}$ | $\left.\begin{array}{ll} \mathrm{Si^{iv}} & \mathrm{O''} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{O''} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{O''} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{O''} \end{array}\right\}$ | $\left.\begin{array}{ll} \mathrm{Si^{iv}} & \mathrm{O''} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{O''} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{O''} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{O''} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{O''} \end{array}\right\}$ | $\left.\begin{array}{ll} \mathrm{Si^{iv}} & \mathrm{O''} \\ & \mathrm{OH} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{O''} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{O''} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{O''} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{O''} \\ & \mathrm{O} \\ \mathrm{Si^{iv}} & \mathrm{OH} \\ & \mathrm{O''} \end{array}\right\}$ | |
| Hexasilicic acid. | 1st Hexasilicic anhydride. | 2nd Hexasilicic anhydride. | 3rd Hexasilicic anhydride. | 4th Hexasilicic anhydride. | 5th Hexasilicic anhydride. | 6th Hexasilicic anhydride. | |
| ..<br>..<br>.. | ..<br>..<br>.. | ..<br>..<br>.. | ..<br>..<br>.. | ..<br>..<br>.. | ..<br>..<br>.. | ..<br>..<br>.. | |
| $\mathrm{Si}^n\mathrm{H}^{2n+2}\mathrm{O}^{3n+1}$ | $\mathrm{Si}^n\mathrm{H}^{2n}\mathrm{O}^{3n}$ | $\mathrm{Si}^n\mathrm{H}^{2n-2}\mathrm{O}^{3n-1}$ | $\mathrm{Si}^n\mathrm{H}^{2n-4}\mathrm{O}^{3n-2}$ | $\mathrm{Si}^n\mathrm{H}^{2n-6}\mathrm{O}^{3n-3}$ | $\mathrm{Si}^n\mathrm{H}^{2n-8}\mathrm{O}^{3n-4}$ | $\mathrm{Si}^n\mathrm{H}^{2n-10}\mathrm{O}^{3n-5}$ | $\mathrm{Si}^n\mathrm{H}^{2n-2m}\mathrm{O}^{3n-m}$ |
| Acid. | First anhydride. | Second anhydride. | Third anhydride. | Fourth anhydride. | Fifth anhydride. | Sixth anhydride. | Nth anhydride. |

SCHOOL OF MEDICINE

In fact, on account of the slight stability of these acids, few of them exist in a free state, but many salts are known which correspond to them. These salts constitute a great part of the numerous mineralogical species whose formulas up to this time appeared so complicated.

By placing the hydrochloric solution of silicic acid in a cylinder open at one end and closed at the other by parchment paper (paper soaked in sulphuric acid, washed and dried), then placing this in water, Mr. Graham has obtained a soluble silicic acid. In this process, which he calls dialysis, the hydrochloric acid and the different crystallizable substances which the solution contained pass through the parchment-paper, and the soluble silicic acid remains in a pure state on the top of this paper. This acid seems to belong to a very condensed type. A very small quantity of potash suffices to saturate it; it is easily destroyed, and is transformed into gelatinous silica. Time alone produces this result.

**Sulphide of Silicon** ($Si^{iv}S^2$).—Sulphide of silicon may be obtained in a pure state by transmitting the vapour of sulphide of carbon over silica heated to redness. Water decomposes it, forming hydrosulphuric acid and a variety of silicic acid which remains dissolved. This phenomenon explains the formation of natural silicious waters.

## CARBON C.

Atomic weight = 12. Molecular weight unknown.

There are many varieties of carbon; these have common properties and distinctive characters.

The common properties are the following:

Carbon is infusible at the highest temperatures and insoluble in all known liquids. At a temperature which varies for each variety, it combines with oxygen, giving rise, according to the quantities of oxygen employed, either to carbonic anhydride ($CO^2$) or to oxide of carbon ($CO$), which are both gaseous.

It has been stated that certain varieties of carbon combine directly with hydrogen under the influence of a strong electric current, forming a hydrocarbon ($C^2H^2$). It is probable that all the varieties of carbon would undergo the same reaction if they all were sufficiently good conductors of electricity.

The known varieties of carbon are: the diamond, graphite, charcoal, animal black, lamp black, burnt sugar, and gas coke. We might also add anthracite, pit coal, and peat charcoal; that is to say, the mineral combustibles; but these being only vegetable bodies more or less carbonized, are far from constituting definite chemical species, and therefore their study is left to naturalists.

**Diamond.**—The diamond is carbon in crystals belonging to the cubic system, which often have 48 facets. These facets have a great tendency to form curves. Diamonds are generally colourless; there are, nevertheless, some that are black, or variously coloured.

Diamond is the hardest known body; crystallized boron approaches the nearest to it in this respect. Its density is from 3·50 to 3·55; it is transparent, and the most refracting of all solid bodies; its constitution has been established by its combustion in oxygen. It has been stated that in this case carbonic anhydride is formed; that is to say, the same compound which is produced when ordinary carbon is burnt. When highly heated, diamonds are transformed into a substance analogous to graphite. They are therefore not formed by fusion at a high temperature. They are found in alluvial earths, probably far from where they were formed, and their natural state gives no indication relative to their mode of formation.

The diamond can be cut by the help of its own dust or of that of crystallized boron.

**Graphite (Plumbago).**—Graphite is that variety of carbon used for making pencils: it exists in a natural state. It may be obtained artificially by slowly cooling melted cast iron holding an excess of carbon in solution. The iron, solidified, leaves the graphite; any iron which it may contain is dissolved by hydrochloric acid.

Graphite may be prepared by means of chloride of carbon by a process analogous to that we described for graphitoidal silicon or boron, but the aluminium must be replaced by iron.

Graphite crystallizes in very brilliant black plates; it is soft enough to leave marks on paper; it has a metallic lustre and burns with difficulty.

Sir B. C. Brodie, by causing an oxidizing mixture composed of nitric acid and chlorate of potassium to act on graphite at 60°, has obtained an acid body whose formula appears to be ($C^{11}H^4O^5$). On comparing this acid with a body obtained by M. Wœhler by means of graphitoid silicon, and which has for formula ($Si^4H^4O^5$), and reflecting on the fact that the acid prepared with graphite cannot be obtained with any other variety of carbon, Brodie admits that this acid answers to the formula ($C^4H^4O^5$). He is obliged by this to attribute to carbon an atomic weight equal to 33, which presents no simple proportion to its ordinary atomic weight. In aid of this hypothesis, Brodie observes that while the specific heats of the different varieties of carbon do not accord with the atomic weight of this body, 12, the specific heat of graphite is in accordance with the atomic weight, 33.

These considerations are very important. Unfortunately, the formula of Sir B. C. Brodie's compound and the analogies between this body and that of M. Wœhler are not established sufficiently for the hypothesis we have just stated to be considered as demonstrated. Nevertheless, the property of giving rise to a compound which can be obtained with no other variety of carbon shows that this metalloid exists in graphite under a particular allotropic state. Consequently, analogy leads us to believe that graphitoidal silicon also represents an allotropic state of silicon.

**Coke.**—Coke is the carbon obtained by calcining pit coal; it is porous, and is not easily combustible: 100 parts of pit coal yield from 60 to 65 parts of coke.

**Wood Charcoal.**—This carbon is prepared either by distilling wood in a closed retort, or by setting fire to large quantities of wood covered with earth. The first method has this advantage, that it allows the volatile products, such as vinegar, wood-spirit, etc., to be collected; but it gives a carbon which is little used. This process ought to be employed when we wish to obtain an easily combustible carbon, as when it is required for the manufacture of gunpowder; but it must not be used when the charcoal is required as fuel for furnaces.

Wood charcoal possesses the property of absorbing gases without combining with them. When it is already saturated with a gas, it is less able to absorb others: therefore, in demonstrating this property, we must begin by calcining the carbon, or by exposing it some time in vacuo, in order to free it from the gases it contains. All gases are not equally absorbed by carbon; those that are most soluble in water are also the most readily absorbed.

The condensation of gases by carbon causes them to enter into reaction more readily. An explosion is produced when a piece of wood charcoal saturated with hydrosulphuric acid gas is brought into contact with oxygen.

This absorbent property of wood charcoal causes it to be employed as a disinfectant, and to be used in medicine as a remedy for flatulence, to absorb the gases which fill the digestive canal.

Wood charcoal also takes up colouring substances of organic origin, and even certain mineral substances, among which is iodine.

**Animal Black.**—This is prepared by calcining bones in closed retorts. This carbon always contains phosphate and carbonate of lime; but by washing it with hydrochloric acid it is freed from these impurities.

Like wood charcoal, animal black absorbs gases and disinfects, but in an inferior degree. On the other hand, it is a much better decolorizer, and is therefore much used, and of great importance in manufactories and sugar refineries.

**Lamp Black.**—Lamp black is prepared by receiving in proper chambers the black smoke resulting from the combustion of resinous or highly carbonaceous substances in presence of an insufficient quantity of oxygen. This carbon is not pure; it must be calcined in a crucible to free it from the tarry matter it contains.

Lamp black constitutes a carbon in very fine powder, and is used to make Indian ink and other black pigments. In pharmacy it is employed in the preparation of black caustic, which is composed of one part of this body and three parts of concentrated sulphuric acid. Lamp black is used to give the sulphuric acid a pasty consistence.

**Carbon of Sugar.**—This is prepared by calcining sugar. It is very spongy; but the walls of the interstices it contains are very compact and brilliant: the result is that sugar carbon has only the appearance of a porous body, and that it has not absorbing properties. It is a very pure carbon.

**Gas Coke.**—The carburetted gases which are disengaged in the preparation of gas used for lighting, partially decompose on contact with the strongly-heated sides of the retort in which the distillation of the pit coal takes place. On these sides a very compact and hard carbon is deposited, which has a metallic lustre, and is a good conductor of heat and electricity. This carbon is employed in the manufacture of certain electric batteries (Bunsen's).

## COMBINATIONS OF CARBON WITH THE METALLOIDS PREVIOUSLY STUDIED.

The combinations of carbon with chlorine, bromine, iodine, and hydrogen will be studied in organic chemistry. We will only speak here of the compounds carbon forms with oxygen and sulphur.

**Oxide of Carbon.**—Carbonic oxide is obtained:—

1st. By burning carbon in an insufficient quantity of oxygen:

$$\underset{\text{Carbon.}}{2C} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} = \underset{\text{Carbonic oxide.}}{2(CO)}$$

2nd. By decomposing carbonic anhydride either by carbon or by red-hot iron:

$$\underset{\text{Carbonic anhydride.}}{(CO^2)} + \underset{\text{Carbon.}}{C} = \underset{\text{Carbonic oxide.}}{2(CO)}$$

$$\underset{\text{Carbonic anhydride.}}{4(CO^2)} + \underset{\text{Iron.}}{3(Fe)} = \underset{\text{Oxide of iron.}}{(Fe^3O^4)} + \underset{\text{Carbonic oxide.}}{4(CO)}$$

3rd. By decomposing by carbon an oxide that is difficult to reduce, such as oxide of zinc:

$$\underset{\text{Oxide of zinc.}}{(ZnO)} + \underset{\text{Carbon.}}{C} = \underset{\text{Carbonic oxide.}}{(CO)} + \underset{\text{Zinc.}}{Zn}$$

4th. By decomposing oxalic acid by bodies having a great affinity for water, like concentrated sulphuric acid. The carbonic oxide is then found mixed with carbonic anhydride, from which it is set free by passing it through a bottle filled with a solution of potash:

$$\underset{\text{Crystallized oxalic acid.}}{\left(C^2H^2O^4 + 2aq.\right)} = \underset{\text{Water.}}{3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Carbonic oxide.}}{\left(CO\right)} + \underset{\text{Carbonic anhydride.}}{\left(CO^2\right)}$$

5th. By heating one part of yellow ferrocyanide of potassium with three parts of sulphuric acid :

$$\underset{\text{Yellow ferrocyanide of potassium.}}{\left(Fe(CN)^6K^4\right)} + \underset{\text{Sulphuric acid.}}{6\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Water.}}{6\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} =$$

$$\underset{\text{Sulphate of iron.}}{\left(\left.\begin{matrix}SO^{2''}\\Fe''\end{matrix}\right\}O^2\right)} + \underset{\text{Sulphate of potassium.}}{2\left(\left.\begin{matrix}SO^{2''}\\K^2\end{matrix}\right\}O^2\right)} + \underset{\text{Sulphate of ammonium.}}{3\left(\left.\begin{matrix}SO^{2''}\\(NH^4)^2\end{matrix}\right\}O^2\right)} + \underset{\text{Carbonic oxide.}}{6\left(CO\right)}$$

Carbonic oxide is a permanent gas without smell or taste, colourless, hardly soluble in water, and of a density of 0·96.

It burns in air with a blue flame, producing carbonic anhydride. Two volumes of carbonic oxide consume one volume of oxygen to become transformed into carbonic anhydride, and the carbonic anhydride produced occupies two volumes. If the composition of carbonic gas be supposed to be known, the composition of oxide of carbon may be deduced. In effect, the weight of carbon contained in a given volume of carbonic anhydride is known. This quantity being the same as that which forms part of an equal volume of carbonic oxide, on subtracting it from the total weight of this gas we learn the weight of the oxygen.

The tendency of carbonic oxide to absorb oxygen renders it a powerful reducing agent.

Exposed to the sun, this gas combines with chlorine, forming an oxychloride (chloride of carbonyl) ($COCl^2$), which decomposes on contact with water into hydrochloric acid and carbonic anhydride :

$$\underset{\text{Oxychloride of carbon.}}{\left(COCl^2\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Carbonic anhydride.}}{\left(CO^2\right)}$$

Carbonic oxide is a very poisonous gas.

**Carbonic Anhydride** ($CO^2$).—Carbonic anhydride is obtained :—

1st. By burning carbon in an excess of oxygen :

$$\underset{\text{Carbon.}}{C} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} = \underset{\text{Carbonic anhydride.}}{\left(CO^2\right)}$$

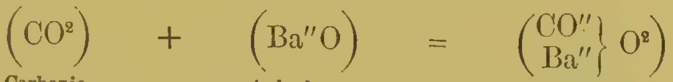
2nd. By decomposing a carbonate by hydrochloric acid. Carbonate of calcium is the one generally employed :

$$\underset{\text{Carbonate of lime.}}{\left(\left.\begin{matrix}CO''\\Ca''\end{matrix}\right\}O^2\right)} + \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\text{Carbonic anhydride.}}{\left(CO^2\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Chloride of calcium.}}{\left(\begin{matrix}Ca''\\Cl^2\end{matrix}\right)}$$

Carbonic anhydride is gaseous at ordinary temperatures and under ordinary pressure. It is liquefied by a pressure of 36 atmospheres. When liquid carbonic anhydride is thrown into the atmosphere, a part immediately vaporizes and absorbs, in consequence, such a quantity of heat that another part passes into the solid state. To collect the latter, the liquid jet is directed into a hemisphere of iron. The carbonic anhydride may be kept solid for some time without its returning to the gaseous state. Pressed between the fingers, it destroys the skin like a hot body. When mixed with ether and placed in the receiver of an air-pump, the temperature is lowered to −100°.

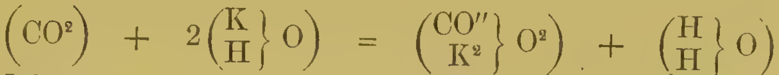
Gaseous carbonic anhydride has a density of 1·529. It may be decanted in the air like a liquid.

Water dissolves its own volume of this gas, but does not combine with it to form an acid; on the contrary, carbonic anhydride combines directly with basic anhydrides to form salts. It also combines with bases; the production of a salt is then accompanied by that of a molecule of water:



$$\left(CO^2\right) + \left(Ba''O\right) = \left(\begin{matrix}CO''\\ Ba''\end{matrix}\right\} O^2\Big)$$

Carbonic anhydride. Anhydrous oxide of barium. Carbonate of barium.



$$\left(CO^2\right) + 2\left(\begin{matrix}K\\ H\end{matrix}\right\} O\Big) = \left(\begin{matrix}CO''\\ K^2\end{matrix}\right\} O^2\Big) + \left(\begin{matrix}H\\ H\end{matrix}\right\} O\Big)$$

Carbonic anhydride. Hydrate of potassium. Carbonate of potassium. Water.

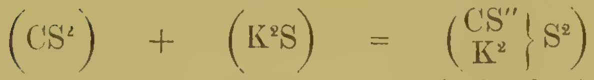
Carbonic anhydride loses half its oxygen when passed over iron or carbon heated to redness. The electric spark decomposes it also into carbonic oxide and oxygen.

Carbonic acid gas does not burn nor support combustion. It also does not support respiration, but it is not nearly so poisonous as carbonic oxide. On injecting it into the different cavities of the body, local anesthesia is produced.

When carbon is burnt in pure oxygen so as to entirely transform the latter into carbonic anhydride, it is observed that the gaseous volume does not vary. If, therefore, from the weight of a given volume of carbonic anhydride that of an equal volume of oxygen be subtracted, the difference will express the weight of carbon contained in this gas.

M. Dumas prefers to operate so as to omit all consideration of volume. He burns a known quantity of pure carbon (diamond) in a current of pure oxygen, and then passes the gases into tubes full of potash, previously weighed, and intended to absorb the carbonic anhydride. On again weighing these tubes after the experiment, the weight of the carbonic anhydride formed is determined, and on subtracting the weight of carbon burnt, the oxygen is known by the difference.

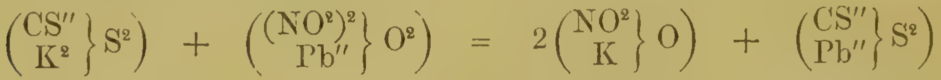
**Sulphide of Carbon** ($CS^2$).—The sulphide of carbon is obtained on passing sulphur in vapour over red-hot carbon. It is a fetid liquid, volatile at 46°. It burns in air with a dull flame, giving carbonic and sulphurous anhydrides. It is an excellent solvent for iodine, sulphur, and phosphorus, and combines with alkaline sulphides (sulphides of potassium or sodium), forming sulpho-salts.



$$(CS^2) + (K^2S) = \left(\left.\begin{matrix}CS''\\K^2\end{matrix}\right\}S^2\right)$$

Sulphide of carbon. Sulphide of potassium. Sulphocarbonate of potassium.

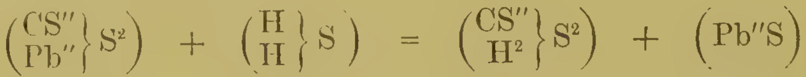
The solution of these alkaline sulpho-salts is precipitated by soluble salts of lead, forming sulphocarbonate of lead.



$$\left(\left.\begin{matrix}CS''\\K^2\end{matrix}\right\}S^2\right) + \left(\left.\begin{matrix}(NO^2)^2\\Pb''\end{matrix}\right\}O^2\right) = 2\left(\left.\begin{matrix}NO^2\\K\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}CS''\\Pb''\end{matrix}\right\}S^2\right)$$

Sulphocarbonate of potassium. Nitrate of lead. Nitrate of potassium. Sulphocarbonate of lead.

Finally, the plombic sulpho-salt, digested in water through which is transmitted a current of hydrosulphuric acid, decomposes into sulphide of lead and sulphocarbonic acid.



$$\left(\left.\begin{matrix}CS''\\Pb''\end{matrix}\right\}S^2\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}S\right) = \left(\left.\begin{matrix}CS''\\H^2\end{matrix}\right\}S^2\right) + (Pb''S)$$

Sulphocarbonate of lead. Hydrosulphuric acid. Sulphocarbonic acid. Sulphide of lead.

Sulphide of carbon is used in gutta-percha manufactures. It softens this substance: its vapours, which are very deleterious, produce serious effects on the workmen who breathe them.

## TIN Sn.

Atomic weight = 118. Molecular weight unknown.

Tin is found in the state of oxide, mixed with sulphide and arsenio-sulphide. The mineral is first roasted in air to transform all into oxides; then it is intimately mixed with carbon and heated. The carbon becomes converted into oxide of carbon, and this reduces the oxide of tin to the state of metallic tin.

$$(SnO^2) + 2(CO) = 2(CO^2) + Sn.$$

Oxide of tin. Oxide of carbon. Carbonic anhydride. Tin.

Malacca tin is very pure.

Tin is silver-white in colour; it is soft and very malleable; it has a crystalline structure, which is shown by causing an acid to act on its surface. The crystals made visible form coloured rings.

Tin cannot be directly pulverized, but it is obtained in powder by melting and stirring it constantly while cooling.

It melts at 228°; it is preserved for an indefinite time in air while cold, but it easily oxidizes when melted, and at a red heat it burns very brightly, giving rise to stannic anhydride ($SnO^2$).

Oxydizing bodies, such as nitric acid or nitrate of potassium, act on tin, producing either metastannic acid ($Sn^5H^{10}O^{15}$), polymeric with stannic acid ($SnH^2O^3$), or stannate of potassium ($SnK^2O^3$).

Tin unites directly with phosphorus, sulphur, chlorine, bromine, and iodine. Hydrochloric acid dissolves tin, disengaging hydrogen and forming protochloride of tin.

$$\underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Tin.}}{Sn} = \underset{\text{Protochloride of tin.*}}{\left.\begin{matrix}Sn''\\Cl^2\end{matrix}\right\}} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}}$$

Differing in this from all the metalloids we have previously studied, tin forms with oxygen an oxide ($SnO$), which is a true basic anhydride, capable of combining directly with acid anhydrides and with acids, forming salts, with the elimination of water. These salts may be recognized by the following characters:

1st. Water decomposes them, forming an insoluble sub salt, while a certain quantity of acid set free, holds in solution a portion of the salt undecomposed.

2nd. Potash added to this solution, causes the formation of a precipitate soluble in an excess of the reagent, but which again becomes deposited when the solution is exposed in vacuo.

3rd. The chloride of gold produces in the solution of these salts a purple-coloured precipitate (the purple of Cassius).

4th. Hydrosulphuric acid gives rise to a brown precipitate, soluble in hydrosulphate of ammonia and in boiling hydrochloric acid, but insoluble in ammonia.

## COMBINATIONS OF TIN WITH METALLOIDS PREVIOUSLY STUDIED.

**Protochloride of Tin** ($SnCl^2$).—This compound is obtained by dissolving tin in hydrochloric acid. It is a crystalline body, and is volatile at a low red heat.

Water decomposes it into hydrochloric acid and oxychloride of tin ($Sn^2Cl^2O$).

$$\underset{\text{Protochloride of tin.}}{2\left(\left.\begin{matrix}Sn''\\Cl^2\end{matrix}\right\}\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Oxychloride of tin.}}{\left(Sn^2Cl^2O\right)} + \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)}$$

The solution of protochloride of tin, heated in presence of hydrochloric acid and sulphurous anhydride, gives rise to a yellow deposit of bisulphide of tin:

$$\underset{\text{Protochloride of tin.}}{6\left(\left.\begin{matrix}Sn\\Cl^2\end{matrix}\right\}\right)} + \underset{\text{Sulphurous anhydride.}}{2\left(SO^2\right)} + \underset{\text{Hydrochloric acid.}}{8\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\text{Bisulphide of tin.}}{\left(SnS^2\right)} + \underset{\text{Tetrachloride of tin.}}{5\left(\left.\begin{matrix}Sn\\Cl^4\end{matrix}\right\}\right)} + \underset{\text{Water.}}{4\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

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* The term *proto*, placed before chloride, does not indicate, as the term *mono* would, that the compound contains a single atom of chlorine, but that it is the least chlorinated of all the compounds which tin can form; it represents the first degree of chlorination of tin.

The protochloride of tin has a strong affinity for chlorine, which transforms it into perchloride of tin, and for oxygen, which transforms it into a mixture of perchloride of tin and stannic acid :

$$\underset{\text{Protochloride of tin.}}{2\left(SnCl^2\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Stannic acid.}}{\left(\left.\begin{matrix}(SnO)''\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Perchloride of tin.}}{\left(SnCl^4\right)}$$

**Perchloride of Tin.**—This body is prepared by passing a current of chlorine in excess over tin gently heated. It is a fuming liquid, which forms with water a crystallizable hydrate ($SnCl^4,5aq$).

Bases decompose it into metallic stannate and chloride :

$$\underset{\text{Perchloride of tin.}}{\left(\left.\begin{matrix}Sn^{iv}\\Cl^4\end{matrix}\right\}\right)} + \underset{\text{Potash.}}{6\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic stannate.}}{\left.\begin{matrix}(SnO'')\\K^2\end{matrix}\right\}O^2} + \underset{\text{Chloride of potassium.}}{4\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)} + \underset{\text{Water.}}{3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

Hydrosulphuric acid added to the solution forms a yellow precipitate of sulphide of tin, soluble in ammonia, in hydrosulphate of ammonia, and in boiling hydrochloric acid.

The chloride of gold does not precipitate it.

**Bromides of Tin.**—The protobromide of tin is prepared like the protochloride, and possesses analogous properties. It is the same with the perbromide.

**Iodides of Tin.**—The protiodide of tin is prepared by the direct combination of one atom of tin and two atoms of iodine. Its properties are analogous to those of the protochloride and the protobromide. The periodide is also obtained by direct synthesis, and possesses similar properties to those of its two congeners.

**Fluorides of Tin.**—Two fluorides of tin are known : the protofluoride ($SnFl^2$) and the perfluoride ($SnFl^4$). These are obtained by treating either the protoxide of tin or stannic anhydride by hydrofluoric acid :

$$\underset{\text{Protoxide of tin.}}{\left(SnO\right)} + \underset{\text{Hydrofluoric acid.}}{2\left(\left.\begin{matrix}H\\Fl\end{matrix}\right\}\right)} = \underset{\text{Protofluoride of tin.}}{\left(SnFl^2\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

$$\underset{\text{Stannic anhydride.}}{\left(SnO^2\right)} + \underset{\text{Hydrofluoric acid.}}{4\left(\left.\begin{matrix}H\\Fl\end{matrix}\right\}\right)} = \underset{\text{Perfluoride of tin.}}{\left(SnFl^4\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

**Protoxide of Tin.**—When protochloride of tin is precipitated by potash, protohydrate of tin is obtained $\left(\left.\begin{matrix}Sn''\\H^2\end{matrix}\right\}O^2\right)$. This body is white and insoluble in water. It can act as a base, that is to say, it can enter into double decomposition with acids, or it can act as an acid, entering into double decomposition with bases :

$$\underset{\text{Hydrate of tin.}}{\left(\left.\begin{matrix}\mathrm{Sn}''\\ \mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right)} + \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}\mathrm{SO}^{2\prime\prime}\\ \mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right)} = \underset{\text{Sulphate of tin.}}{\left(\left.\begin{matrix}\mathrm{SO}^{2\prime\prime}\\ \mathrm{Sn}''\end{matrix}\right\}\mathrm{O}^2\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}$$

$$\underset{\text{Hydrate of tin.}}{\left(\left.\begin{matrix}\mathrm{Sn}''\\ \mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right)} + \underset{\text{Potash.}}{2\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\substack{\text{Stannite of}\\ \text{potassium.}}}{\left(\left.\begin{matrix}\mathrm{Sn}''\\ \mathrm{K}^2\end{matrix}\right\}\mathrm{O}^2\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}$$

The aqueous solution of stannite of potassium, left in vacuo, deposits black crystals of anhydrous oxide of tin, which decrepitate when heated and are transformed into small laminæ of an olive colour. The same solution, submitted to the action of heat, becomes transformed into stannate of potassium and tin, which is precipitated:

$$\underset{\substack{\text{Stannite of}\\ \text{potassium.}}}{2\left(\left.\begin{matrix}\mathrm{Sn}''\\ \mathrm{K}^2\end{matrix}\right\}\mathrm{O}^2\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\substack{\text{Stannate of}\\ \text{potassium.}}}{\left.\begin{matrix}(\mathrm{SnO})''\\ \mathrm{K}^2\end{matrix}\right\}\mathrm{O}^2} + \underset{\text{Potash.}}{2\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Tin.}}{\mathrm{Sn}}$$

Hydrate of tin boiled with an excess of ammonia loses water, and there remains anhydrous protoxide of tin of an olive colour:

$$\underset{\text{Hydrate of tin.}}{\left(\left.\begin{matrix}\mathrm{Sn}''\\ \mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right)} = \underset{\substack{\text{Anhydrous}\\ \text{protoxide of tin.}}}{\left(\mathrm{SnO}\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}$$

When the protochloride of tin is precipitated by an excess of ammonia, in which it is boiled for a short time, and the mass dried without separating the hydrochlorate of ammonia formed, a protoxide of tin is obtained of a fine red colour. This oxide becomes olive on friction.

Protoxide of tin is therefore polymorphous, and the most stable of its three forms is that in which it has an olive colour.

**Stannic Anhydride** ($\mathrm{SnO}^2$) (*Stannic and Metastannic Acids*).—Stannic anhydride is formed when stannic and metastannic acids are strongly calcined. It constitutes a white mass, insoluble in water, and capable of forming stannates when heated with an excess of potash or soda.

**Stannic Acid** $\left(\left.\begin{matrix}(\mathrm{SnO})''\\ \mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right)$.—This acid is none other than the first anhydride of the unknown acid $\left(\left.\begin{matrix}\mathrm{Sn}^{\mathrm{IV}}\\ \mathrm{H}^4\end{matrix}\right\}\mathrm{O}^4\right)$. It is obtained by precipitating the stannates by hydrochloric acid:

$$\underset{\substack{\text{Stannate of}\\ \text{potassium.}}}{\left(\left.\begin{matrix}(\mathrm{SnO})''\\ \mathrm{K}^2\end{matrix}\right\}\mathrm{O}^2\right)} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{2\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{Cl}\end{matrix}\right\}\right)} = \underset{\text{Stannic acid.}}{\left(\left.\begin{matrix}(\mathrm{SnO})''\\ \mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right)} + \underset{\substack{\text{Chloride of}\\ \text{potassium.}}}{2\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{Cl}\end{matrix}\right\}\right)}$$

It is a white gelatinous body, soluble in dilute nitric and sulphuric acids.

Under the influence of a gentle heat it becomes transformed into a polymeric body, metastannic acid:

$$\underset{\text{Stannic acid.}}{5\left(\left.\begin{matrix}(\mathrm{SnO})''\\ \mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right)} = \underset{\text{Metastannic acid.}}{\left.\begin{matrix}(\mathrm{SnO})^5\\ \mathrm{H}^{10}\end{matrix}\right\}\mathrm{O}^{10}}$$

MEDICINE

At a red heat it loses its water, and is transformed into stannic anhydride.

It combines with bases giving salts, the formula of which is:

$$\left(\left.\begin{matrix}(SnO)''\\ MH\end{matrix}\right\}O^2\right)$$

**Metastannic Acid** $\left(\left.\begin{matrix}(SnO)^5\\ H^{10}\end{matrix}\right\}O^{10}\right)$.—This is the first anhydride of the unknown pentastannic acid $\left(\left.\begin{matrix}Sn^5\\ H^{12}\end{matrix}\right\}O^{16}\right)$.

It is obtained by heating tin with nitric acid:

$$\underset{\text{Tin.}}{15Sn} + \underset{\text{Water.}}{5\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)} + \underset{\text{Nitric acid.}}{20\left(\left.\begin{matrix}NO^2\\ H\end{matrix}\right\}O\right)} = \underset{\text{Metastannic acid.}}{3\left(\left.\begin{matrix}(SnO)^5\\ H^{10}\end{matrix}\right\}O^{10}\right)} + \underset{\text{Binoxide of nitrogen.}}{20(NO)}$$

Metastannic acid is a white crystalline body, insoluble in water, and in dilute nitric and sulphuric acids; it dissolves in hydrochloric acid and in concentrated sulphuric acid. Water does not precipitate it from its solutions.

When it has been prepared by means of nitric acid, it is insoluble in ammonia; but if it has been precipitated from the solution of one of its salts by means of an acid, it dissolves readily in this alkali.

With bases it forms salts whose formula is $\left(\left.\begin{matrix}(SnO)^5\\ H^8\\ M^2\end{matrix}\right\}O^{10}\right)$.

Heated with an excess of base, these salts are transformed into stannates.

**Sulphides of Tin.**—There are two sulphides of tin: the protosulphide (SnS), and the bisulphide ($SnS^2$).

Both these may be obtained by transmitting a current of sulphuretted hydrogen into the corresponding chlorides:

$$\underset{\text{Perchloride of tin.}}{\left(\left.\begin{matrix}Sn^{iv}\\ Cl^4\end{matrix}\right\}\right)} + \underset{\text{Sulphuretted hydrogen.}}{2\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}S\right)} = \underset{\text{Bisulphide of tin.}}{\left(Sn^{iv}S^2\right)} + \underset{\text{Hydrochloric acid.}}{4\left(\left.\begin{matrix}H\\ Cl\end{matrix}\right\}\right)}$$

$$\underset{\text{Protochloride of tin.}}{\left(\left.\begin{matrix}Sn\\ Cl^2\end{matrix}\right\}\right)} + \underset{\text{Sulphuretted hydrogen.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}S\right)} = \underset{\text{Protosulphide of tin.}}{\left(SnS\right)} + \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\ Cl\end{matrix}\right\}\right)}$$

Bisulphide of tin may also be prepared by heating a mixture of 12 parts of tin amalgamated with 6 parts of mercury, 7 of sulphur, and 6 of chloride of ammonium, until complete evaporation of the mercury and the chloride of ammonium takes place.

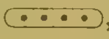
The two sulphides of tin can be combined with alkaline sulphides, producing sulpho-salts.

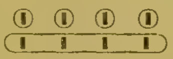
### ZIRCONIUM—TITANIUM—THORINUM.

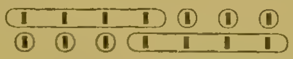
These bodies are too rare, and of too slight importance to be studied in detail in this work. Their properties place them by the side of the preceding metalloids.

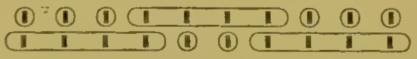
## GENERAL REMARKS ON TETRATOMIC METALLOIDS.

The simple bodies of this family, being tetratomic, ought to be able to combine at most with four monatomic radicles, forming compounds which correspond to the formula $(R^{iv}X^4)$. Moreover, as polyatomic radicles have the power of accumulating in molecules, the simple bodies of this family may form with monatomic radicles an indefinite number of compounds containing any quantity of these latter, inferior to four atoms for one of the tetratomic body.

Let us, like M. Kékulé, for example, represent a tetratomic atom by the figure , and a monatomic atom by the figure ⊙, we may conceive:

1st. That a tetratomic atom may be saturated by four monatomic atoms 

2nd. That two tetratomic atoms may be saturated by six monatomic atoms, the two tetratomic atoms partially saturating each other 

3rd. That three tetratomic atoms may be saturated by eight monatomic atoms 

In a word, that a group formed by any number of tetratomic atoms requires for its saturation a number of monatomic atoms equal to double the number of tetratomic atoms + 2. Thus, on designating by R the tetratomic radicle, and by X the monatomic radicle, we shall have for all the possible saturated compounds of these two radicles the general formula $R^n = X^{2n+2n}$, without being able up to the present time to fix the limits of the values of *n*.*

As every saturated body may lose a part of its elements giving rise to incomplete molecules, we may further conceive that each of the com-

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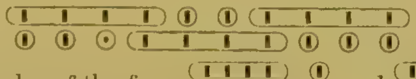
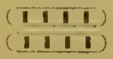
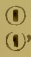
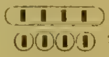
* In order that a body shall really exist, it is not sufficient that the atoms which constitute it possess the number of centres of attraction without which the grouping would be impossible; elective affinities are also necessary, able to determine the stability of the grouping. If, for example, three tetratomic atoms and eight monatomic atoms had less tendency to form a single molecule of the form



than to form three molecules of the form  , and , it is evident that the group $R^{vi3}X'^{8}$ would never be produced.

pounds corresponding to the preceding general formula may lose successively 1, 2, 3, 4, 5....*n* molecules of the monatomic element, thereby forming new non-saturated compounds. (When the monatomic element these bodies have lost is hydrogen, M. Lourenço calls them anhydrogenides.)

Between carbon and hydrogen, for example, all the following combinations are theoretically possible :—

| SATURATED COMPOUNDS. | NON-SATURATED COMPOUNDS. | | | | |
|---|---|---|---|---|---|
| $C H^4$ | $C H^2$ | .. .. | .. .. | .. .. | .. .. .. .. |
| $C^2 H^6$ | $C^2 H^4$ | $C^2 H^2$ | .. .. | .. .. | .. .. .. .. |
| $C^3 H^8$ | $C^3 H^6$ | $C^3 H^4$ | $C^3 H^2$ | .. .. | .. .. .. .. |
| $C^4 H^{10}$ | $C^4 H^8$ | $C^4 H^6$ | $C^4 H^4$ | $C^4 H^2$ | .. .. .. .. |
| $C^5 H^{12}$ | $C^5 H^{10}$ | $C^5 H^8$ | $C^5 H^6$ | $C^5 H^4$ | $C^5 H^{4-2m}$ |
| $C^6 H^{14}$ | $C^6 H^{12}$ | $C^6 H^{10}$ | $C^6 H^8$ | $C^6 H^6$ | $C^6 H^{6-2m}$ |
| $C^7 H^{16}$ | $C^7 H^{14}$ | $C^7 H^{12}$ | $C^7 H^{10}$ | $C^7 H^8$ | $C^7 H^{8-2m}$ |
| $C^8 H^{18}$ | $C^8 H^{16}$ | $C^8 H^{14}$ | $C^8 H^{12}$ | $C^8 H^{10}$ | $C^8 H^{10-2m}$ |
| $C^9 H^{20}$ | $C^9 H^{18}$ | $C^9 H^{16}$ | $C^9 H^{14}$ | $C^9 H^{12}$ | $C^9 H^{12-2m}$ |
| $C^{10}H^{22}$ | $C^{10}H^{20}$ | $C^{10}H^{18}$ | $C^{10}H^{16}$ | $C^{10}H^{14}$ | $C^{10}H^{14-2m}$ |
| .. .. | .. .. | .. .. | .. .. | .. .. | .. .. .. .. |
| .. .. | .. .. | .. .. | .. .. | .. .. | .. .. .. .. |
| .. .. | .. .. | .. .. | .. .. | .. .. | .. .. .. .. |
| .. .. | .. .. | .. .. | .. .. | .. .. | .. .. .. .. |
| .. .. | .. .. | .. .. | .. .. | .. .. | .. .. .. .. |
| $C^nH^{2n+2}$ | $C^nH^{2n}$ | $C^nH^{2n-2}$ | $C^nH^{2n-4}$ | $C^nH^{2n-6}$ | $C^nH^{2n-6-2m}$ |

A series of analogous combinations may equally be imagined between carbon and simple or compound monatomic radicles other than hydrogen; and similar series in which, instead of carbon, the other tetratomic metalloids, that is to say, silicon, zirconium, tin, and titanium take part.

In reality these series, with the exception of the carbon group, are very little known. Of the latter, most of the hydrogenized compounds contained in the preceding table can be prepared, and also the corresponding chlorine and bromine compounds.

As to silicon, we only know silicated hydrogen ($SiH^4$), and the chloride, bromide, and fluoride of silicon :

$$(SiCl^4),(SiBr^4) \quad \text{and} \quad (SiFl^4)$$

Up to the present time no hydrogenized compound has been prepared either of tin, zirconium, or titanium. The chlorides ($SnCl^2$), ($SnCl^4$); bromides ($SnBr^2$), ($SnBr^4$); and the fluorides of tin ($SnFl^2$), ($SnFl^4$), are known, as well as a chloride of zirconium ($ZrCl^4$); the two saturated chlorides of titanium ($TiCl^4$) and ($TiCl^6$), and the fluoride of the same body ($TiFl^4$).

All the metalloids of this family are capable of uniting with the biatomic metalloids. Each of them forms two oxides and two sulphides, which answer to the formulas $(R^{iv}X'')$ and $(R^{iv}X''^{2})$. But the protoxide of silicon is not known with certainty, and the protoxide of zirconium and the protosulphides of carbon and titanium are not known at all. On the contrary, a sesquioxide of titanium $(Ti^{2}O^{3})$ has been prepared, corresponding to the chloride $(Ti^{2}Cl^{6})$.

The sulphides of these bodies can all form sulpho-salts by combination with alkaline sulphides.

The binoxides are all acid anhydrides; those of zirconium and thorium, nevertheless, can act as basic anhydrides. As to the protoxides, they sometimes act as basic anhydrides, sometimes both as basic and acid anhydrides, and sometimes they do not act as either.

## FIFTH GROUP (PENTATOMIC METALLOIDS).

### NITROGEN $\left.\begin{matrix}N\\N\end{matrix}\right\}$

Atomic weight = 14. Molecular weight = 28.

Nitrogen constitutes about four-fifths of the atmospheric air; it is prepared:

1st. By leaving phosphorus at the ordinary temperature in a bell-glass full of air until the gaseous volume no longer diminishes, which indicates that all the oxygen is absorbed.

2nd. By burning phosphorus under a bell-glass full of air, and placed over a water bath; the phosphoric anhydride which forms by the consumption of the oxygen of the air is dissolved in water in the state of metaphosphoric acid, and nitrogen nearly pure remains in the glass.

3rd. By transmitting a current of air slowly through a tube heated to dull redness and full of copper filings; the oxygen is fixed by the metal, and the gas which comes out of the apparatus is pure nitrogen, and may be collected as soon as the air which fills the tube containing the copper has been expelled.

4th. By causing chlorine to act on an aqueous solution of ammonia:

$$\underset{\text{Ammonia.}}{8\left(NH^{3}\right)} + \underset{\text{Chlorine.}}{3\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}\right)} = \underset{\text{Chloride of ammonium.}}{6\left(NH^{4}Cl\right)} + \underset{\text{Nitrogen.}}{\left.\begin{matrix}N\\N\end{matrix}\right\}}$$

The general mode of conducting the operation is to cause a current of gaseous chlorine to pass into a Woulf's bottle with three tubulures, half full of ammonia, and then to collect the gas which comes out of the bottle. Care must be taken to maintain the ammonia always in great excess, or the reaction of the chlorine on the chloride of ammonium would give rise to chloride of nitrogen, a very explosive body, which might occasion very serious accidents.

5th. By boiling a solution of nitrite of ammonium; water and free nitrogen are produced:

$$\underset{\text{Nitrite of ammonium.}}{\left(\left.\begin{matrix}\mathrm{NO}\\ \mathrm{NH^4}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\text{Water.}}{2\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Nitrogen.}}{\left.\begin{matrix}\mathrm{N}\\ \mathrm{N}\end{matrix}\right\}}$$

Nitrogen is a permanent gas, colourless, inodorous, and tasteless. Its density is 0·972; water only dissolves $\frac{25}{1000}$ of its volume. It does not burn nor support combustion. Though not poisonous, animals and plants die in it, through being deprived of oxygen.

Nitrogen only combines directly with oxygen when this latter body has been previously transformed into ozone by the electric spark, or by some other means. But still the presence of a powerful base seems necessary for the combination to take place.

Nitrogen combines directly with boron and titanium at a red heat.

It also combines at a red heat with carbon when this body has been previously mixed with carbonate of potassium or sodium. In this case a compound is formed whose formula is (CNK), *the cyanide of potassium.*

Hydrogen only combines indirectly with nitrogen.

In certain mines pure nitrogen is produced in consequence of the oxidation by air of sulphide of iron and sulphide of copper existing there.

## COMBINATIONS OF NITROGEN WITH THE METALLIODS PREVIOUSLY STUDIED.

**Ammonia** ($NH^3$).—When azotized organic matters are calcined or left to putrefy; or, to speak more generally, every time that nitrogen and hydrogen meet in a nascent state in presence of an acid, salts are produced which answer to the formula ($NH^4R$), R being any radicle whatever. These salts distilled in the presence of a base liberate ammonia in the gaseous state:

$$\underset{\text{Chloride of ammonium.}}{2\left(\mathrm{NH^4Cl}\right)} + \underset{\text{Hydrate of lime.}}{\left(\left.\begin{matrix}\mathrm{Ca''}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{O^2}\right)} = \underset{\text{Chloride of calcium.}}{\left(\left.\begin{matrix}\mathrm{Ca''}\\ \mathrm{Cl^2}\end{matrix}\right\}\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Ammonia.}}{2\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{N}\right)}$$

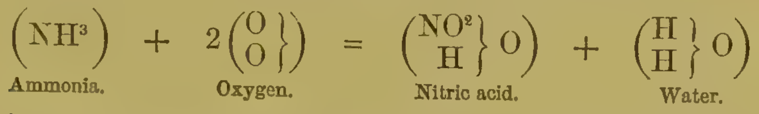
The gas is transmitted through a tube full of fragments of caustic potash, which absorbs the water formed in the preceding reaction, and the gas is afterwards collected in a bell-glass placed over mercury.

Ammonia is gaseous at the ordinary temperature and under the ordinary pressure, but it liquefies at a low temperature or under great pressure; it may also be obtained as a white translucent solid, fusible at —75°.

In the gaseous state ammonia is colourless and has a pungent odour; its density is 0·591. Water dissolves about 500 times its volume.

At a low red heat, or under the influence of a series of electric sparks, ammoniacal gas decomposes into its elements; in this case it is observed that the gaseous volume augments one half.

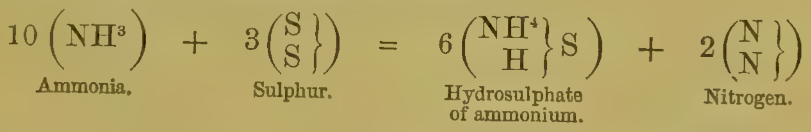
Ammoniacal gas extinguishes combustion. It does not burn in air, but it burns in pure oxygen, giving rise to water and free nitrogen; if a current of mixed ammoniacal gas and oxygen be directed on to spongy platinum, water and nitric acid are produced:



$$\underset{\text{Ammonia.}}{\left(NH^3\right)} + \underset{\text{Oxygen.}}{2\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\right)} = \underset{\text{Nitric acid.}}{\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

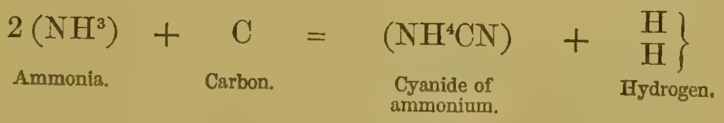
Chlorine and bromine react with ammonia, giving hydrochloric or hydrobromic acid and free nitrogen. With iodine an explosive compound is obtained.

At a high temperature sulphur acts on ammonia, producing hydrosulphate of ammonium and free nitrogen:



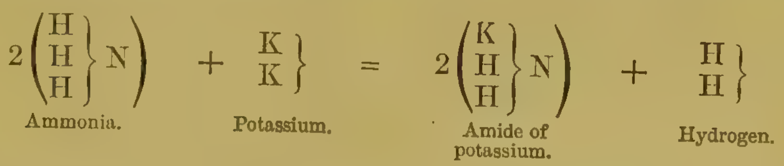
$$\underset{\text{Ammonia.}}{10\left(NH^3\right)} + \underset{\text{Sulphur.}}{3\left(\left.\begin{matrix}S\\S\end{matrix}\right\}\right)} = \underset{\text{Hydrosulphate of ammonium.}}{6\left(\left.\begin{matrix}NH^4\\H\end{matrix}\right\}S\right)} + \underset{\text{Nitrogen.}}{2\left(\left.\begin{matrix}N\\N\end{matrix}\right\}\right)}$$

At a red heat carbon transforms ammonia into cyanide of ammonium:



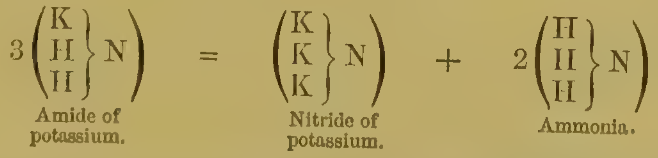
$$\underset{\text{Ammonia.}}{2\left(NH^3\right)} + \underset{\text{Carbon.}}{C} = \underset{\text{Cyanide of ammonium.}}{\left(NH^4CN\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}}$$

Alkaline metals, heated in a current of ammoniacal gas, are substituted for an atom of the hydrogen contained in this body, and give compounds known as amides:



$$\underset{\text{Ammonia.}}{2\left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right)} + \underset{\text{Potassium.}}{\left.\begin{matrix}K\\K\end{matrix}\right\}} = \underset{\text{Amide of potassium.}}{2\left(\left.\begin{matrix}K\\H\\H\end{matrix}\right\}N\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}}$$

At a greater heat these products divide into ordinary ammonia and trimetallic nitride:



$$\underset{\text{Amide of potassium.}}{3\left(\left.\begin{matrix}K\\H\\H\end{matrix}\right\}N\right)} = \underset{\text{Nitride of potassium.}}{\left(\left.\begin{matrix}K\\K\\K\end{matrix}\right\}N\right)} + \underset{\text{Ammonia.}}{2\left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right)}$$

At a still higher temperature these nitrides divide into metal and free nitrogen:

$$\underset{\text{Nitride of potassium.}}{2\left(K^3N\right)} = \underset{\text{Potassium.}}{3\left(\left.\begin{matrix}K\\K\end{matrix}\right\}\right)} + \underset{\text{Nitrogen.}}{\left.\begin{matrix}N\\N\end{matrix}\right\}}$$

Ammoniacal gas colours the reddened tincture of litmus blue, and combines directly with acids forming salts. This property is owing to the pentatomicity of nitrogen, which tends to become saturated, forming compounds of the ($NX^5$) type. Ammoniacal gas also combines with acid anhydrides. But the products arising thus have none of the characteristic properties of salts. (See *Amides.*)

Ammoniacal salts present very great analogies, both in their crystalline forms and in their reactions, to alkaline salts. These analogies may be explained by placing among these salts the group ($NH^4$) (ammonium), which acts as a compound monatomic electro-positive radicle. All the objections that have been made to this hypothesis are removed by the theory of the atomicity of elements.

If sal-ammoniac be decomposed by the galvanic current in presence of mercury, on plunging the negative electrode into this liquid, the mercury is observed to swell considerably. If the pasty mass that forms be distilled, it decomposes into mercury, ammonia, and hydrogen. It is also observed that for one molecule of ammonia liberated, one atom of hydrogen becomes disengaged. The galvanic current therefore decomposes the chloride of ammonium ($NH^4,Cl$) into chlorine and ammonium ($NH^4$), as it decomposes the chloride of sodium into chlorine and sodium, and if the ammonium does not remain isolated when the mercury is evaporated it is only because it is instable in a free state.

The preceding mercurial compound may also be obtained by decomposing the chloride of ammonium by the amalgam of potassium or sodium, the alkaline metal then directly displaces the ammonium. This mercurial compound ought to be considered as an amalgam of ammonium.

The aqueous solution of ammonia is much used: it is obtained by transmitting a current of ammoniacal gas into Woulf's apparatus, and has received the name of liquid ammonia. When it is heated, the gas it contains becomes wholly disengaged.

In medicine, liquid ammonia is used to produce rapid blisters. A dose of a few drops is also taken internally as a remedy for intoxication. It has been recommended for croup. The acetate of ammonia (Mindererus' spirit) is very useful as a stimulant diaphoretic and an emmenagogue.

**Chloride, Bromide, and Iodide of Nitrogen.**—When chlorine acts on ammoniacal salts in aqueous solution, a liquid is formed, the composition of which answers to the formula ($NCl^3$).

This liquid can react on bromide of potassium, producing a bromide of nitrogen ($NBr^3$).

Free iodine also reacts on ammonia, giving a nitrogenized product which appears to have a constitution varying according to the mode of its preparation. According to M. Stahlschmidt, the compound obtained by the action of an alcoholic solution of iodine on aqueous ammonia, would have ($NI^3$) for formula, and that obtained by treating an alcoholic solution of iodine by an alcoholic solution of ammonia would answer to the formula ($NI^2H$).

The chlorides, bromides, and iodides of nitrogen are very explosive bodies, dangerous to handle.

### COMPOUNDS OF NITROGEN WITH OXYGEN.

The compounds of nitrogen with oxygen are:

Protoxide of nitrogen ($N^2O$).

Binoxide of nitrogen ($NO$).

Nitrous anhydride ($N^2O^3$), and the nitrites corresponding to it ($NMO^2$).

Hyponitride $NO^2$. (Peroxide of nitrogen).

Nitric anhydride $N^2O^5$, and the nitrates corresponding to it ($NMO^3$).

**Protoxide of Nitrogen** $N^2O$ is obtained:—

1st. By heating dry nitrate of ammonium in a glass retort:

$$\underset{\substack{\text{Nitrate of}\\\text{ammonium.}}}{\left(\left.\begin{matrix}NO^2\\NH^4\end{matrix}\right\}O\right)} = \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\substack{\text{Protoxide of}\\\text{nitrogen.}}}{\left(N^2O\right)}$$

2nd. By heating a nitrosulphate:

$$\underset{\substack{\text{Nitrosulphate}\\\text{of potassium.}}}{\left(SN^2K^2O^5\right)} = \underset{\substack{\text{Sulphate of}\\\text{potassium.}}}{\left(\left.\begin{matrix}SO^{2''}\\K^2\end{matrix}\right\}O^2\right)} + \underset{\substack{\text{Protoxide}\\\text{of nitrogen.}}}{\left(N^2O\right)}$$

3rd. By leaving for some time a mixture of sulphurous anhydride and binoxide of nitrogen in water, and then absorbing the excess of sulphurous anhydride by potash:

$$\underset{\substack{\text{Sulphurous}\\\text{anhydride.}}}{\left(SO^2\right)} + \underset{\substack{\text{Binoxide}\\\text{of nitrogen.}}}{2\left(NO\right)} + \underset{\text{Water.}}{\left(H^2O\right)} = \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)} + \underset{\substack{\text{Protoxide}\\\text{of nitrogen.}}}{\left(N^2O\right)}$$

4th. By leaving binoxide of nitrogen on moistened iron filings; the iron absorbs half the oxygen of the binoxide of nitrogen, which is thus transformed into protoxide:

$$\underset{\substack{\text{Binoxide of}\\\text{nitrogen.}}}{4(NO)} = \underset{\substack{\text{Protoxide of}\\\text{nitrogen.}}}{2(N^2O)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}}$$

The protoxide of nitrogen is a colourless and inodorous gas, with a slightly sweetish taste. Water dissolves four-fifths of its volume. Its density is 1·527. It is liquefied at 0° under the pressure of 30 atmospheres: in a liquid state it is very volatile, boils at −88° and gives voluminous crystals when evaporated in vacuo. On evaporation it causes so great a reduction in the temperature, that alcohol in contact with it becomes so viscous that it does not run out when the vessel containing it is inverted.

The protoxide of nitrogen is unstable; it readily surrenders its oxygen to combustible bodies. Thus the combustion of organic matters, of sulphur, phosphorus, and hydrogen takes place in this gas even more actively than in air, owing to the greater proportion of oxygen contained in it. A piece of carbon burns on contact with liquid protoxide of nitrogen.

When protoxide of nitrogen is breathed it produces a species of intoxication. It usually causes uncontrollable spasmodic laughter; hence it is popularly named "laughing gas."

This gas may be analyzed by heating a known volume in a curved bell-glass with a globule of sodium. The metal takes the oxygen, and there remains a volume of nitrogen equal to the volume of the protoxide employed.

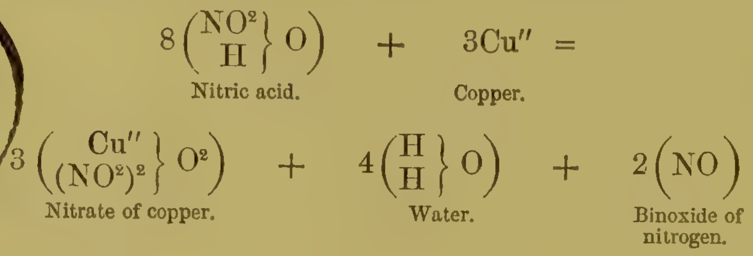
| | |
|---|---|
| If from the density of the protoxide of nitrogen . | 1·527 |
| the density of nitrogen be subtracted . . . . | 0·977 |
| there remains . . . | 0·550 |

which approaches the half of the density of oxygen: two volumes of protoxide of nitrogen therefore contain two volumes of nitrogen and one volume of oxygen united, with condensation of one-third.

**Binoxide of Nitrogen** (NO) may be prepared :—

1st. By causing nitric acid to act on copper in a bottle with two tubulures similar to that used in preparing hydrogen:

EEDS
HOOL OF
DICINE



$$8\underset{\text{Nitric acid.}}{\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)} + \underset{\text{Copper.}}{3Cu''} =$$
$$3\underset{\text{Nitrate of copper.}}{\left(\left.\begin{matrix}Cu''\\(NO^2)^2\end{matrix}\right\}O^2\right)} + 4\underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + 2\underset{\text{Binoxide of nitrogen.}}{(NO)}$$

2nd. By causing a diluted acid to act on a nitrite. The nitrous acid which forms is divided, on contact with water, into nitric acid and binoxide of nitrogen. The water takes no part in the reaction, though its presence is necessary:

$$\underset{\text{Nitrous acid.}}{3(NHO^2)} = \underset{\text{Binoxide of nitrogen.}}{2(NO)} + \underset{\text{Nitric acid.}}{(NHO^3)} + \underset{\text{Water.}}{(H^2O)}$$

3rd. By heating a mixture of protochloride of iron, hydrochloric acid, and nitrate of potassium:

$$\underset{\text{Protochloride of iron.}}{6\left(\left.\begin{matrix}\mathrm{Fe}''\\\mathrm{Cl}^2\end{matrix}\right\}\right)} + \underset{\text{Hydrochloric acid.}}{8\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\text{Nitrate of potassium.}}{2\left(\left.\begin{matrix}\mathrm{NO}^2\\\mathrm{K}\end{matrix}\right\}\mathrm{O}\right)} =$$

$$\underset{\text{Perchloride of iron.}}{3\left(\left.\begin{matrix}\mathrm{Fe}^2\\\mathrm{Cl}^6\end{matrix}\right\}\right)} + \underset{\text{Chloride of potassium.}}{2\left(\left.\begin{matrix}\mathrm{K}\\\mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\text{Water.}}{4\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Binoxide of nitrogen.}}{2(\mathrm{NO})}$$

The binoxide of nitrogen is a permanent colourless gas; its density is 1·039: it dissolves in 20 times its volume of water. It does not possess the property of producing an acid when brought into contact with water, nor of forming salts on contact with bases, it is therefore not an acid anhydride.

This gas combines directly with the oxygen of the air, producing reddish vapours of hyponitride:

$$\underset{\text{Binoxide of nitrogen.}}{2(\mathrm{NO})} + \underset{\text{Oxygen.}}{\left.\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right\}} = \underset{\text{Hyponitride.}}{2(\mathrm{NO}^2)}$$

If the quantity of oxygen present be only equal to one volume for four volumes of binoxide of nitrogen, hyponitride is no longer produced, but nitrous anhydride is formed:

$$\underset{\text{Binoxide of nitrogen.}}{4(\mathrm{NO})} + \underset{\text{Oxygen.}}{\left.\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right\}} = \underset{\text{Nitrous anhydride.}}{2(\mathrm{N}^2\mathrm{O}^3)}$$

The binoxide of nitrogen decomposes at red heat into hyponitride and free nitrogen:

$$\underset{\text{Binoxide of nitrogen.}}{4(\mathrm{NO})} = \underset{\text{Nitrogen.}}{\left.\begin{matrix}\mathrm{N}\\\mathrm{N}\end{matrix}\right\}} + \underset{\text{Hyponitride.}}{2(\mathrm{NO}^2)}$$

It dissolves in a solution of protosulphate of iron. This solution, which is of a clear green colour, becomes a reddish brown, which deepens more and more as the absorption progresses; if potash be afterwards added and it be heated, ammonia is formed, and the protoxide of iron passes to the state of sesquioxide.

The solutions of manganate and permanganate of potassium also absorb the binoxide of nitrogen.

Though possessing more oxygen than the protoxide, the binoxide of nitrogen, owing to its greater stability, is less combustible than the first of these gases. Nevertheless, bodies having great affinity for oxygen, such as phosphorus or carbon, burn brightly when they are lighted and placed in it.

Binoxide of nitrogen is analyzed by the same process as the protoxide, and we thus find that two volumes of this gas contain equal volumes of nitrogen and oxygen united without condensation.

**Nitrous Anhydride** ($N^2O^3$) **and Nitrites** ($NMO^2$).—Nitrous anhydride is prepared:

1st. By passing into a cold receiver a mixture of four volumes of binoxide of nitrogen and one volume of oxygen.

2nd. By decomposing hyponitride by water at a low temperature:

$$\underset{\text{Hyponitride.}}{4\left(NO^2\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Nitric acid.}}{2\left(NHO^3\right)} + \underset{\text{Nitrous anhydride.}}{\left(N^2O^3\right)}$$

Nitrous anhydride constitutes a blue liquid, which is very volatile and very unstable, boiling at about 0°.

In presence of water and at an ordinary temperature, it decomposes into binoxide of nitrogen and nitric acid, according to the equation:

$$\underset{\text{Nitrous anhydride.}}{3\left(N^2O^3\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Binoxide of nitrogen.}}{4\left(NO\right)} + \underset{\text{Nitric acid.}}{2\left(NHO^3\right)}$$

Nitrites are obtained by heating nitrates. The nitrites of potassium and sodium especially are easily obtained by this means. They are well-defined salts.

The nitrite of ammonium is decomposed by a very slight heat into water and free nitrogen. The analysis of nitrous anhydride has not been made directly, its composition is deduced from that of the nitrites.

**Hyponitride** ($NO^2$).—This is obtained:

1st. By passing a mixture of two volumes of binoxide of nitrogen and one volume of oxygen into a very cold receiver.

2nd. By decomposing perfectly dry nitrate of lead by heat, and receiving the products of the decomposition in a cold receiver:

$$\underset{\text{Nitrate of lead.}}{2\left(Pb''\left\{\begin{matrix}ONO^2\\ONO^2\end{matrix}\right.\right)} = \underset{\text{Oxide of lead.}}{2\left(PbO\right)} + \underset{\text{Hyponitride.}}{4\left(NO^2\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}}$$

Hyponitride is solid below 9°: above that it assumes a liquid state up to 22°, at which temperature it boils. From 0 to 22°, its colour, which was light yellow, becomes darker; its vapour is a deep reddish brown. The density of this vapour is 1·72.

Hyponitride reddens litmus paper, but this effect does not belong to it; it is the result of its decomposition by the bases contained in the tincture of litmus.

Bases and basic anhydrides transform hyponitride into a mixture of nitrate and nitrite.

$$\underset{\text{Hyponitride.}}{2\left(NO^2\right)} + \underset{\text{Hydrate of potassium.}}{2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Nitrite of potassium.}}{\left(\left.\begin{matrix}NO\\K\end{matrix}\right\}O\right)} + \underset{\text{Nitrate of potassium.}}{\left(\left.\begin{matrix}NO^2\\K\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

Water also decomposes it into nitric acid and nitrous anhydride:

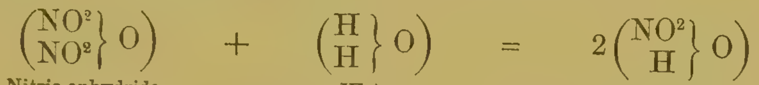
but on account of the instability of this latter body, nitric acid and binoxide of nitrogen are produced at the ordinary temperature. The following is the definite equation:

$$\underset{\text{Hyponitride.}}{3(NO^2)} + \underset{\text{Water.}}{(H^2O)} = \underset{\text{Nitric acid.}}{2(NHO^3)} + \underset{\text{Binoxide of nitrogen.}}{(NO)}$$

But we must observe that the production of the binoxide of nitrogen being consecutive to that of nitrous anhydride, all the terms of the preceding equation must be doubled.

Hyponitride may be analyzed by weighing a certain quantity of it, then vaporizing it, and passing this vapour over red-hot copper filings. The oxygen is fixed by the metal, and the nitrogen set free is collected in a graduated tube, where it is measured, and the oxygen calculated from the difference.

**Nitric Anhydride** $\left(\left.\begin{matrix}NO^2\\NO^2\end{matrix}\right\}O\right)$.—Nitric anhydride, which was long unknown, has been obtained by M. Deville, who prepared it by transmitting a current of perfectly dry chlorine over equally well-dried nitrate of silver at a temperature of 95°. It is a solid body, crystallized in prisms of the third system, fusible at 30° and volatile at 47°. It is very unstable. In presence of water it enters into double decomposition, and becomes transformed into nitric acid:



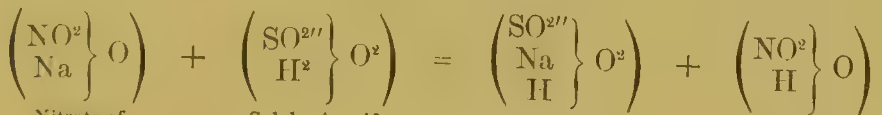
$$\underset{\text{Nitric anhydride.}}{\left(\left.\begin{matrix}NO^2\\NO^2\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Nitric acid.}}{2\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)}$$

It is analyzed by reducing a known weight to vapour, and passing this over red-hot copper filings, which retain the oxygen: the nitrogen is collected and the proportion ascertained by measuring the volume.

**Nitric Acid** $\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)$.—When a mixture of oxygen and nitrogen is submitted to the action of a succession of electric sparks in presence of a solution of hydrate of potassium, the oxygen becomes ozonized, and reacts on the nitrogen and the potash, forming nitrate of potassium.

These nitrates form whenever organic matters are decomposed in air at a temperature of 20° or 30°, in presence of water and alkaline carbonates. In Peru there exist considerable layers of nitrate of sodium.

Nitric acid is obtained by distilling these salts with a quantity of sulphuric acid sufficient to transform their metal into acid sulphate:



$$\underset{\text{Nitrate of sodium.}}{\left(\left.\begin{matrix}NO^2\\Na\end{matrix}\right\}O\right)} + \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2\prime\prime}\\H^2\end{matrix}\right\}O^2\right)} = \underset{\text{Acid sulphate of sodium.}}{\left(\left.\begin{matrix}SO^{2\prime\prime}\\Na\\H\end{matrix}\right\}O^2\right)} + \underset{\text{Nitric acid.}}{\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)}$$

If half the sulphuric acid only were employed, the reaction would still take place, but greater heat would be requisite, and part of the nitric acid would be decomposed.

The acid is purified by distilling it over nitrate of lead, which retains the sulphuric acid evolved in the first process; the first portion of the product, which contains hyponitride, being rejected.

Normal nitric acid thus obtained is a colourless pungent liquid; it is very corrosive, and colours the skin yellow, destroying it; its density is 1·552 at 20°. It boils at 86° and freezes at $-49°$.

In the light, a portion of the acid decomposes into hyponitride—which colours it yellow—oxygen and water. This water combines with the undecomposed acid, and increases its stability.

A similar decomposition is observed when nitric acid is distilled. It commences to boil at 86°, but as it boils it partly decomposes, and the water formed combines with the undecomposed portion, whose boiling point it elevates. Thus the temperature gradually rises up to 123°, where it remains; the liquid which then passes over answers to the formula $((NHO^3)^2 + 3aq.)$. This is a definite hydrate, much more stable than the normal acid, and constitutes the ordinary nitric acid of commerce.

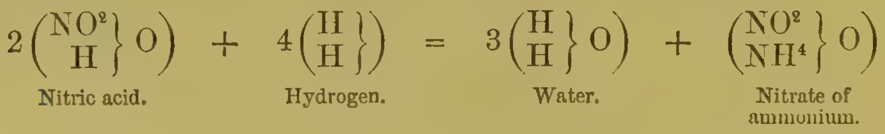
With the exception of oxygen, chlorine, bromine, and nitrogen, all the metalloids decompose nitric acid, taking a part of its oxygen. An acid then forms which is derived from the metalloid employed, or, in some rare cases, a basic oxide which produces a salt on contact with an excess of nitric acid, as takes place with bismuth and zirconium.

Nitric acid acts on all metals except gold, platinum, iridium, rhodium, and ruthenium. The metals take a part of its oxygen and are transformed into basic oxides, which in presence of the undecomposed acid give metallic nitrates.

In these reactions binoxide of nitrogen is disengaged, but in reality it is nitrous acid that first arises, and then on contact with water decomposes into nitric acid and binoxide of nitrogen.

It is a remarkable fact that the normal acid acts less easily on metals than the hydrate $((NHO^3)^2 + 3aq.)$. This seems to be owing to the fact that the nitrous acid produced in the reaction does not meet with sufficient water for its decomposition when the normal acid is used.

In all these reactions there is always the decomposition of a certain quantity of water with production of hydrogen. This latter, in a nascent state, transforms a portion of the nitric acid into nitrate of ammonium.



$$\underset{\text{Nitric acid.}}{2\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)} + \underset{\text{Hydrogen.}}{4\left(\left.\begin{matrix}H\\H\end{matrix}\right\}\right)} = \underset{\text{Water.}}{3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Nitrate of ammonium.}}{\left(\left.\begin{matrix}NO^2\\NH^4\end{matrix}\right\}O\right)}$$

Normal nitric acid acts very strongly on certain organic substances; water is produced, and a compound which by its composition represents the primitive substance in which the monatomic radicle $(NO^2)$ is substituted for a part of the hydrogen:

$$\underset{\text{Benzine.}}{\left(C^6H^6\right)} + \underset{\text{Nitric acid.}}{\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)} = \underset{\text{Nitrobenzine.}}{\left(C^6H^5(NO^2)\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

This phenomenon is called nitrous substitution.

When nitric acid is mixed with hydrochloric acid, and the mixture is heated, a reaction takes place, water is formed, and at the same time binoxide of nitrogen and chlorine are liberated:

$$\underset{\text{Nitric acid.}}{2\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)} + \underset{\text{Hydrochloric acid.}}{6\left(HCl\right)} = \underset{\text{Water.}}{4\left(H^2O\right)} + \underset{\text{Binoxide of nitrogen.}}{2\left(NO\right)} + \underset{\text{Chlorine.}}{3\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}\right)}$$

If the liquid contain only the preceding mixture, the binoxide of nitrogen and the chlorine combine, and the compounds discovered by Gay-Lussac, and improperly known as chloronitrous acid . $(NOCl)$
and hypochloronitric acid . $(NOCl^2)$,
are obtained.

If, on the contrary, the mixture of the two acids contain another body, a metal or a metalloid, this body takes possession of the nascent chlorine and is dissolved in the state of chloride, or it becomes oxidized at the cost of the water, whose hydrogen combines with the chlorine. Analogous phenomena are observed when hydrobromic or hydriodic acid is substituted for the hydrochloric acid.

The mixture of hydrochloric and nitric acids, possessing the property of dissolving gold, has received the name of "aqua regia."

The composition of nitric acid is deduced from that of nitrate of lead. If a known weight of this salt be strongly calcined, there remains pure oxide of lead, which is weighed, and from its weight that of the lead which the nitrate contained is deduced. On the other hand, another known weight of nitrate of lead is decomposed by heat in a tube which contains copper turnings, the nitrogen is set free, and its volume measured.

If from the weight of the nitrate of lead that of the nitrogen and lead be deducted, there remains that of the oxygen.

Finally, a certain quantity of nitric acid is weighed and is entirely transformed into nitrate of lead by heating it with litharge: from the weight of the nitrate produced we deduce that of the nitrogen as well as that of the oxygen which the salt contains, and which in consequence the first nitric acid would contain, and then on subtracting their weight from that of this acid we learn the proportion of the hydrogen by the difference.

## PHOSPHORUS $\left.\begin{matrix}P^2\\P^2\end{matrix}\right\}$

**Atomic weight = 31. Molecular weight = 124.**

Phosphorus is procured from bone ash, in which it exists in the state of neutral phosphate of calcium $\left(\left.\begin{matrix}(PO''')^2\\Ca''^3\end{matrix}\right\}O^6\right)$, along with carbonate of calcium.

To extract the phosphorus, the bone ash is digested with sulphuric acid for twenty-four hours, when insoluble sulphate of calcium, and biacid phosphate of calcium soluble in water are formed, as well as carbonic anhydride, which is disengaged.

$$\text{1st.}\ \left(\left.\begin{matrix}CO''\\Ca''\end{matrix}\right\}O^2\right) + \left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right) = \left(\left.\begin{matrix}SO^{2''}\\Ca''\end{matrix}\right\}O^2\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + \left(CO^2\right)$$

Carbonate of calcium. Sulphuric acid. Sulphate of calcium. Water. Carbonic anhydride.

$$\text{2nd.}\ \left(\left.\begin{matrix}(PO'')^2\\Ca''^3\end{matrix}\right\}O^6\right) + 2\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right) = 2\left(\left.\begin{matrix}SO^{2''}\\Ca''\end{matrix}\right\}O^2\right) + \left(\left.\begin{matrix}(PO''')^2\\Ca''\\H^4\end{matrix}\right\}O^6\right)$$

Neutral phosphate of calcium. Sulphuric acid. Sulphate of calcium. Biacid phosphate of calcium.

After twenty-four hours the mixture is treated with water and filtered. The filtered liquor is first evaporated to the consistence of a syrup, and then mixed with powdered charcoal and evaporated to dryness. Finally, this mass is pulverized and placed in an earthenware retort which is heated to redness. Pyrophosphate of calcium, which remains in the retort, and phosphoric acid are produced. This latter, on contact with red-hot carbon, gives oxide of carbon, hydrogen, and phosphorus in vapour which are brought into a cold receiver. The final reaction may be explained by the following equation:

$$4\left[\left.\begin{matrix}(PO''')^2\\Ca''\\H^4\end{matrix}\right\}O^6\right] + 10C = 2\left[\left.\begin{matrix}(PO''')^2\\Ca''^2\end{matrix}\right\}O^5\right] + 10(CO) + 8\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + P^4$$

Biacid phosphate of calcium. Carbon. Pyrophosphate of calcium. Oxide of carbon. Water. Phosphorus.

The equation is written in this manner although all the members may be divided by two, because the molecule of phosphorus containing four atoms, the smallest quantity of this body that can become free, corresponds to $P^4$.

To purify the phosphorus, it is tied up in wash-leather and squeezed in water warmed to 50° or 60°. The phosphorus melts and passes through the pores of the wash-leather, which retains the impurities.

Finally, a workman draws into a tube by suction the phosphorus melted under water, and places the tube in cold water, where the phosphorus is solidified in a stick and removed from the tube.

If the phosphorus be required perfectly pure, it ought to be distilled in an atmosphere of hydrogen gas.

Ten years ago it was proposed to extract phosphorus from bone ash by heating a mixture of this ash and carbon in a current of hydrochloric

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acid gas. This process, which would possess the advantage of giving the whole of the phosphorus contained in the bones, has however not yet been applied. Phosphorus is solid at the ordinary temperature; it melts at 44° and boils at 290°. Its vapour density is 4·32; from which the weight of its molecule is deduced to be 124, which indicates that this molecule contains four atoms, the atomic weight of phosphorus being 31. The density of solid phosphorus is 1·83.

Phosphorus is sufficiently soft to be marked by the nail: water does not dissolve it; alcohol and ether dissolve a small quantity, and sulphide of carbon dissolves it freely: its solution in the latter solvent submitted to spontaneous evaporation deposits the phosphorus in rhombic dodecahedra.

Phosphorus is yellow and transparent; left under water, it becomes covered with a white layer formed of a number of microscopic crystals.

It has so great an affinity for oxygen that it combines with this metalloid at the ordinary temperature. If there be much phosphorus, the heat disengaged may suffice to cause ignition. Nevertheless, in perfectly dry oxygen, the combination does not take place unless the gas has only a very slight pressure. On account of its inflammability, phosphorus ought to be kept under water and handled with very great caution. It is luminous in the dark. It is not yet quite certain that this production of light is the effect of slow combustion.

Phosphorus does not combine directly either with nitrogen or hydrogen; it combines readily with chlorine, bromine, iodine, and sulphur; its combination with chlorine and bromine is attended with combustion; when combined with sulphur, unless the operation be conducted under water, it may give rise to dangerous explosions.

Phosphorus is a powerful poison; a small dose excites the organs of generation violently.

**Allotropic Modification of Phosphorus.**—Exposed to the direct light of the sun, or, what is better, heated for several hours in an inert gas, such as carbonic acid, to a temperature of 235—250 degrees, phosphorus undergoes an important modification. It becomes red, opaque, insoluble in sulphide of carbon and solvents in general, and its density becomes 2. It may be kept in air without being oxidized, and only ignites at 250°. At 230° it combines with sulphur without explosion; its affinity for chlorine, iodine, and bromine, is less than when it is in the ordinary state.

Until lately red phosphorus was considered as incapable of being crystallized; but quite recently it has been found that when heated in a tube hermetically sealed it is sublimed before melting, and gives greyish crystals, isomorphous with those of arsenic. Red phosphorus would, therefore, correspond to the normal state of arsenic.

Amorphous phosphorus is not poisonous, perhaps because it does not oxidize. Ordinary phosphorus, indeed, seems not to be poisonous of itself, but to act by the products of oxidation to which it gives rise.

### COMBINATIONS OF PHOSPHORUS WITH MONATOMIC METALLOIDS.

There are three phosphuretted hydrogens: one gaseous ($PH^3$): another liquid, to which the formula ($PH^2$) is usually given, but which, I think, ought to be represented by the double formula ($P^2H^4$); the third solid, ordinarily written ($P^2H$), but which, in my opinion, ought also to have its formula doubled.

**Gaseous Phosphuretted Hydrogen** ($PH^3$).—This is obtained :—

1st. By causing hydrochloric acid to act on phosphide of calcium or any other metallic phosphide :

$$\underset{\text{Phosphide of calcium.}}{\left(\left.\begin{matrix}\mathrm{P}'''^{2}\\ \mathrm{Ca}''^{3}\end{matrix}\right\}\right)} + 6\underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{Cl}\end{matrix}\right\}\right)} = 3\underset{\text{Chloride of calcium.}}{\left(\left.\begin{matrix}\mathrm{Ca}''\\ \mathrm{Cl}^{2}\end{matrix}\right\}\right)} + 2\underset{\text{Phosphuretted hydrogen.}}{\left(\left.\begin{matrix}\mathrm{P}'''\\ \mathrm{H}^{3}\end{matrix}\right\}\right)}$$

2nd. By heating phosphorus with water and a base, such as potash or lime: the operation is performed by means of an apparatus represented by fig. 27 :

$$\underset{\text{Phosphorus.}}{\mathrm{P}^4} + 3\underset{\text{Potash.}}{\left(\mathrm{KHO}\right)} + 3\underset{\text{Water.}}{\left(\mathrm{H^2O}\right)} = 3\underset{\text{Hypophosphite of potassium.}}{\left(\mathrm{PH^2KO^2}\right)} + \underset{\text{Phosphuretted hydrogen.}}{\left(\left.\begin{matrix}\mathrm{P}'''\\ \mathrm{H}^{3}\end{matrix}\right\}\right)}$$

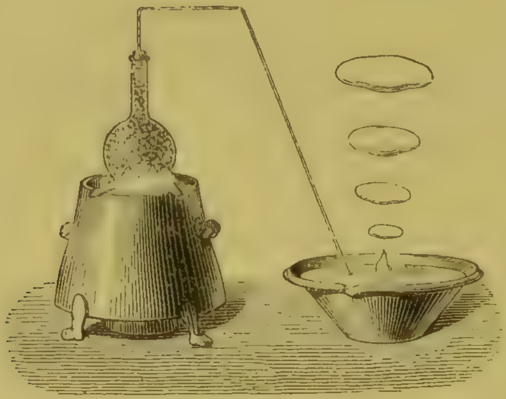


Fig. 27.

3rd. By treating with water the impure phosphides of calcium or barium which are prepared by passing phosphorus in vapour over lime or baryta heated to redness. Phosphuretted hydrogen, a hypophosphite, and free hydrogen, are produced. Probably the equation of this reaction is the following :—

$$2\underset{\text{Phosphide of calcium.}}{\left(\mathrm{P^2Ca''^3}\right)} + 14\underset{\text{Water.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}$$

$$= \underset{\text{Hypophosphite of calcium.}}{\left((\mathrm{PH^2O^2})^2\mathrm{Ca}''\right)} + 2\underset{\text{Phosphuretted hydrogen.}}{\left(\mathrm{PH^3}\right)} + 5\underset{\text{Hydrate of of calcium.}}{\left(\left.\begin{matrix}\mathrm{Ca}''\\ \mathrm{H}^{2}\end{matrix}\right\}\mathrm{O}^2\right)} + 4\underset{\text{Hydrogen.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\right)}$$

4th. By distilling phosphorous acid in a glass retort: perfectly pure phosphuretted hydrogen is disengaged, and a residue of phosphoric acid is left:

$$\underset{\text{Phosphorous acid.}}{4\left(PH^3O^3\right)} = \underset{\text{Phosphuretted hydrogen.}}{\left(\left.\begin{matrix}P'''\\ H^3\end{matrix}\right\}\right)} + \underset{\text{Phosphoric acid.}}{3\left(PH^3O^4\right)}$$

Gaseous phosphuretted hydrogen is nearly insoluble in water, but it readily dissolves in alcohol and ether; its density is 1·185. It is highly inflammable; and on burning deposits red phosphorus, unless it be mixed with oxygen, in which case it explodes on contact with a lighted body, and burns without leaving any residue.

Chlorine decomposes it into hydrochloric acid and chloride of phosphorus.

Binoxide of nitrogen communicates directly to it the property of igniting in air, on account of the elevation of temperature which takes place when the binoxide combines with the oxygen of the air.

Phosphuretted hydrogen, prepared by phosphide of calcium—or by a base, water, and phosphorus—also possesses the property of igniting spontaneously; but this is owing to the circumstance of its containing a small quantity of vapour of liquid phosphuretted hydrogen. It combines directly with hydrobromic or hydriodic acids, forming the crystallized compounds ($PH^4Br$) and ($PH^4I$), which correspond to the bromide and iodide of ammonium. Water and bases decompose these salts, reforming phosphuretted hydrogen.

The chlorides of tin, titanium, antimony, etc., form with phosphuretted hydrogen crystallizable compounds which water decomposes.

To analyze this gas, a known volume is passed into two red-hot tubes from which the air has been removed; the first of these contains copper filings, and the second the oxide of the same metal; the phosphorus is fixed by the copper in the first tube, the increase in the weight of which marks the weight of this metalloid; while the hydrogen is transformed into water in the second tube. This liquid is received into a U-shaped tube full of pumice-stone saturated with sulphuric acid, and previously weighed; the increase in the weight indicates that of the water, and thence that of the hydrogen is deduced.

Thus we find that phosphuretted hydrogen contains in a hundred parts:

| | |
|---|---|
| Phosphorus . . . . . . . . . . . | 91·18 |
| Hydrogen . . . . . . . . . . | 8·82 |
| | 100·00 |

**Liquid Phosphide of Hydrogen** ($P^2H^4$). — When phosphuretted hydrogen obtained by the action of bases and water on phosphorus, or by the action of water on the phosphide of calcium, is placed in a very cold receiver, liquid phosphide of hydrogen is condensed.

This body is spontaneously inflammable, and a trace of its vapour is sufficient to communicate this property to combustible gases, such as hydrogen, oxide of carbon, and gaseous phosphuretted hydrogen.

The presence of an acid causes it to decompose into gaseous and solid phosphides of hydrogen :

$$\underset{\text{Liquid phosphide of hydrogen.}}{5(P^2H^4)} = \underset{\text{Gaseous phosphuretted hydrogen.}}{6(PH^3)} + \underset{\text{Solid phosphide of hydrogen.}}{(P^4H^2)}$$

We have doubled the ordinary formula employed for liquid phosphide of hydrogen, because with the old formula it would represent a radicle of uneven atomicity, and with about two exceptions radicles of uneven atomicity cannot exist without becoming doubled, and besides it is possible that the true formula is a multiple of $(P^2H^4)$.

The determination of the vapour density of the compound can alone decide the question.

**Solid Phosphide of Hydrogen** $(P^4H^2)$.—This is obtained in considerable quantities by receiving in hydrochloric acid the gaseous phosphuretted hydrogen containing the liquid phosphide, collecting on a filter the powder which is deposited, and drying it at 100° after well washing it in water.

Solid phosphide of hydrogen is yellow and insoluble in water; it is not phosphorescent; at 160° it takes fire, and at 180° it decomposes into phosphorus and hydrogen.

We have doubled its formula for a reason analogous to that which caused us to double that of the liquid phosphide.

**Chlorides, Bromides, and Iodides of Phosphorus.**—When a current of dry chlorine is transmitted over an excess of phosphorus placed in a tubulated retort, and gently heated (fig. 28), the phosphorus burns in

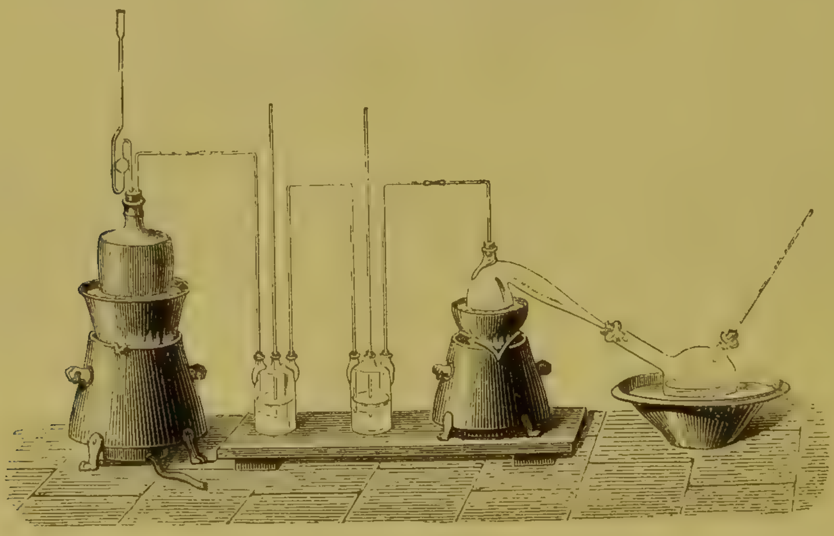


Fig. 28.

the chlorine, and a liquid is distilled, which is colourless, volatile at 78°, and which has for formula $(PCl^3)$; it is the protochloride of phosphorus.

This liquid when dry, and exposed to the action of a current of chlorine, becomes transformed into a solid mass, answering to the formula $(PCl^5)$, which boils at 148°. This is the perchloride of phosphorus.

On contact with water the protochloride of phosphorus gives rise to hydrochloric and phosphorous acids:

$$\underset{\text{Protochloride of phosphorus.}}{\left(PCl^3\right)} + \underset{\text{Water.}}{3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Hydrochloric acid.}}{3\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Phosphorous acid.}}{\left(\left.\begin{matrix}P'''\\H^3\end{matrix}\right\}O^3\right)}$$

When the water is in excess the perchloride becomes transformed into phosphoric and hydrochloric acids:

$$\underset{\text{Perchloride of phosphorus.}}{\left(PCl^5\right)} + \underset{\text{Water.}}{4\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Hydrochloric acid.}}{5\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Phosphoric acid.}}{\left(\left.\begin{matrix}PO''\\H^3\end{matrix}\right\}O^3\right)}$$

But if the quantity of water be insufficient to effect the complete decomposition, it simply exchanges two atoms of chlorine for one atom of oxygen, and gives oxychloride of phosphorus $(PCl^3O)$.

$$\underset{\text{Perchloride of phosphorus.}}{\left(PCl^5\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Oxychloride of phosphorus.}}{\left(PCl^3O\right)}$$

This oxychloride may also be obtained by the direct action of oxygen on the perchloride at a high temperature; chlorine is disengaged.

On causing sulphuretted hydrogen instead of water to act on perchloride of phosphorus, a chlorosulphide of phosphorus $(PCl^3S)$ is obtained, which is simply the preceding body with the oxygen replaced by sulphur.

By dissolving one atomic proportion of phosphorus in sulphide of carbon, adding to the solution three atomic proportions of bromine, and evaporating the sulphide of carbon, there remains liquid protobromide of phosphorus answering to the formula $(PBr^3)$, and precisely analogous to the protochloride in its properties.

If bromine be added to this product, a solid perbromide $(PBr^5)$ is obtained, which can form compounds similar to those formed by the perchloride.

Iodine also forms two compounds with phosphorus, but they differ from the preceding: the protiodide has for formula $(PI^2)$, or what is better $(P^2I^4)$, and the periodide $(PI^3)$.

On contact with water the periodide becomes transformed into hydriodic and phosphorus acids, by a reaction similar to that we described in the case of the protochloride.

As on contact with water the protiodide disengages hydriodic acid without depositing phosphorus, it is probable that in this reaction there is also formed a mixture of phosphorous and hypophosphorous acids:

$$\underset{\text{Protoiodide of phosphorus.}}{\left(\mathrm{P^2I^4}\right)} + 5\underset{\text{Water.}}{\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\text{Phosphorous acid.}}{\left(\left.\begin{matrix}\mathrm{P'''}\\\mathrm{H^3}\end{matrix}\right\}\mathrm{O^3}\right)} + \underset{\text{Hypophosphorous acid.}}{\left(\mathrm{PH^3O^2}\right)} + 4\underset{\text{Hydriodic acid.}}{\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{I}\end{matrix}\right\}\right)}$$

The chlorides, bromides, and iodides of phosphorus are frequently used in organic chemistry. They are useful in procuring the replacement of oxygen by chlorine, bromine, or iodine.

## OXYGENIZED COMPOUNDS OF PHOSPHORUS.

There are three oxy-acids of phosphorus: hypophosphorous acid ($\mathrm{PH^3O^2}$), phosphorous acid ($\mathrm{PH^3O^3}$), and phosphoric acid ($\mathrm{PH^3O^4}$). The phosphorous and phosphoric anhydrides are also known.

**Hypophosphorous Acid** $\left(\mathrm{PO'''}\left\{\begin{matrix}\mathrm{H^2}\\\mathrm{OH}\end{matrix}\right.\right) = (\mathrm{PH^3O^2})$. — We have seen that when phosphorus is heated with potash, lime, or baryta in presence of water, phosphuretted hydrogen is disengaged, while a hypophosphite of the base used remains in solution.

On decomposing hypophosphite of barium by dilute sulphuric acid, separating the sulphate of barium by filtration, and evaporating the filtered liquid to the consistence of a syrup, hypophosphorous acid is obtained, which answers to the formula ($\mathrm{PH^3O^2}$); but of the three atoms of hydrogen it contains only one can be replaced by a metal. To explain this fact, M. Lieben has proposed to give to hypophosphorous acid the rational formula $\left(\left.\begin{matrix}\mathrm{POH^{2\prime}}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)$, or $\left(\mathrm{PO'''}\left\{\begin{matrix}\mathrm{H^2}\\\mathrm{OH}\end{matrix}\right.\right)$

This acid has a great affinity for oxygen: it reduces sulphuric acid, and many metallic oxides; heated in the absence of air, it leaves a residue of phosphoric acid, and disengages gaseous phosphuretted hydrogen mixed with a little liquid phosphide:

$$\underset{\text{Hypophosphorous acid.}}{2(\mathrm{PH^3O^2})} = \underset{\text{Phosphoric acid.}}{(\mathrm{PH^3O^4})} + \underset{\text{Phosphuretted hydrogen.}}{(\mathrm{PH^3})}$$

The liquid phosphide must arise from a secondary reaction.

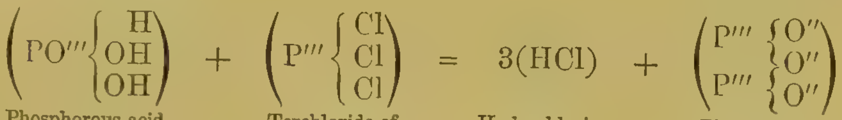
**Phosphorous Acid.**—Phosphorous acid is obtained by dissolving protochloride of phosphorus in water and evaporating at a gentle heat to get rid of the hydrochloric acid and the excess of water. The temperature must not be too high, because the phosphorous acid would decompose into phosphuretted hydrogen and phosphoric acid. (*See* phosphuretted hydrogen.)

Phosphorous acid has such a reducing power that it decomposes sulphurous anhydride into sulphur and oxygen.

In presence of bases, phosphorous acid only exchanges two atoms of hydrogen for metals. M. Lieben proposed on account of this to give it the formula $\left(\left.\begin{matrix}\mathrm{POH''}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{O^2}\right)$, or what is the same thing $\left(\mathrm{PO'''}\left\{\begin{matrix}\mathrm{H}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\right.\right)$

M. Railton has succeeded in replacing the three atoms of hydrogen of phosphorous acid by ethyl. The triethylic phosphite ought to be written $\left(\mathrm{PO'''}\left\{\begin{matrix}\mathrm{C^2H^5}\\ \mathrm{OC^2H^5}\\ \mathrm{OC^2H^5}\end{matrix}\right.\right)$

Phosphorous anhydride is known. This body is formed when phosphorus is oxidized at a low temperature in a volume of oxygen insufficient to transform this metalloid into phosphoric anhydride. It is also produced when the terchloride of phosphorus is made to act on phosphorous acid.



$$\left(\mathrm{PO'''}\left\{\begin{matrix}\mathrm{H}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\right.\right) + \left(\mathrm{P'''}\left\{\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right.\right) = 3(\mathrm{HCl}) + \left(\begin{matrix}\mathrm{P'''} & \left\{\mathrm{O''}\right.\\ & \mathrm{O''}\\ \mathrm{P'''} & \left\{\mathrm{O''}\right.\end{matrix}\right)$$

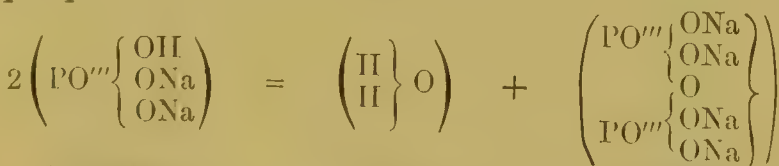
Phosphorous acid. Terchloride of phosphorus. Hydrochloric acid. Phosphorous anhydride.

**Phosphoric Anhydride** ($\mathrm{P^2O^5}$).—When phosphorus is burned in a current of dry air a white powder possessing a great affinity for water is produced, the formula of which is $\mathrm{P^2O^5}$. This is phosphoric anhydride.

**Phosphoric Acid** $\left(\mathrm{PO'''}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\right.\right)$.—When phosphoric anhydride is dissolved in water and the solution is boiled a double decomposition takes place, and if the excess of water be driven off by evaporation there remains a syrup-like liquid answering to the formula $\left(\mathrm{PO'''}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\right.\right)$, which is phosphoric acid.

This acid is triatomic and tribasic: on reacting with bases it can form two series of acid salts and one series of neutral salts.

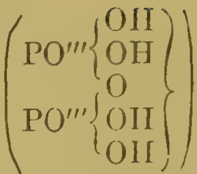
When acid phosphates of the form $\left(\mathrm{PO'''}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OR}\\ \mathrm{OR}\end{matrix}\right.\right)$, such as the sodic phosphate of commerce, are strongly calcined, a molecule of water is eliminated and a salt of a condensed acid is produced, the biphosphoric or pyrophosphoric acid:



$$2\left(\mathrm{PO'''}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{ONa}\\ \mathrm{ONa}\end{matrix}\right.\right) = \left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right) + \left(\begin{matrix}\mathrm{PO'''}\left\{\begin{matrix}\mathrm{ONa}\\ \mathrm{ONa}\end{matrix}\right.\\ \mathrm{O}\\ \mathrm{PO'''}\left\{\begin{matrix}\mathrm{ONa}\\ \mathrm{ONa}\end{matrix}\right.\end{matrix}\right)$$

Acid phosphate of sodium. Water. Pyrophosphate of sodium.

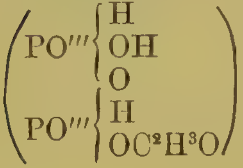
from this salt pyrophosphoric acid may be procured



$$\left(\left.\begin{array}{l}\mathrm{PO'''}\left\{\begin{array}{l}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{O}\end{array}\right.\\ \mathrm{PO'''}\left\{\begin{array}{l}\mathrm{OH}\\ \mathrm{OH}\end{array}\right.\end{array}\right\}\right).$$

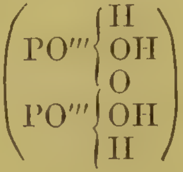
For this purpose it is sufficient to precipitate it by acetate of lead, and to decompose by sulphuretted hydrogen the precipitate of pyrophosphate of lead, after having previously well washed it.

Several chemists opposed to the atomic theory objected to write pyrophosphoric acid ($P^2H^4O^7$). They wished to write it $PH^2O^7$, making $O = 8$. M. Mentschoukine has demonstrated that the formula ($P^2H^4O^7$) alone is correct. This chemist, by causing the chloride of acetyl to act on phosphorous acid, has obtained the monacetic derivative



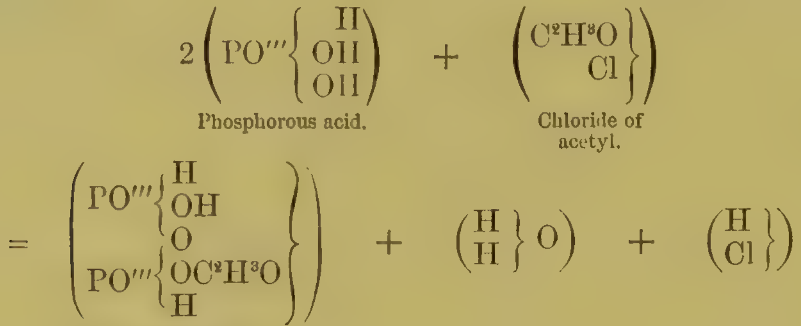
$$\left(\begin{array}{l}\mathrm{PO'''}\left\{\begin{array}{l}\mathrm{H}\\ \mathrm{OH}\\ \mathrm{O}\end{array}\right.\\ \mathrm{PO'''}\left\{\begin{array}{l}\mathrm{H}\\ \mathrm{OC^2H^3O}\end{array}\right.\end{array}\right)$$

of the unknown pyrophosphorous acid, the formula of which would be



$$\left(\begin{array}{l}\mathrm{PO'''}\left\{\begin{array}{l}\mathrm{H}\\ \mathrm{OH}\\ \mathrm{O}\end{array}\right.\\ \mathrm{PO'''}\left\{\begin{array}{l}\mathrm{OH}\\ \mathrm{H}\end{array}\right.\end{array}\right);$$

it forms in accordance with the following equation :



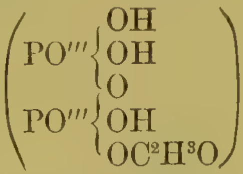
$$2\left(\mathrm{PO'''}\left\{\begin{array}{l}\mathrm{H}\\ \mathrm{OH}\\ \mathrm{OH}\end{array}\right.\right) + \left(\left.\begin{array}{r}\mathrm{C^2H^3O}\\ \mathrm{Cl}\end{array}\right\}\right)$$

Phosphorous acid. Chloride of acetyl.

$$= \left(\left.\begin{array}{l}\mathrm{PO'''}\left\{\begin{array}{l}\mathrm{H}\\ \mathrm{OH}\\ \mathrm{O}\end{array}\right.\\ \mathrm{PO'''}\left\{\begin{array}{l}\mathrm{OC^2H^3O}\\ \mathrm{H}\end{array}\right.\end{array}\right\}\right) + \left(\left.\begin{array}{l}\mathrm{H}\\ \mathrm{H}\end{array}\right\}\mathrm{O}\right) + \left(\left.\begin{array}{l}\mathrm{H}\\ \mathrm{Cl}\end{array}\right\}\right)$$

Aceto-pyrophosphorous acid. Water. Hydrochloric acid.

This aceto-pyrophosphorous acid submitted to oxidation fixes a molecule of oxygen, and is transformed into aceto-pyrophosphoric acid

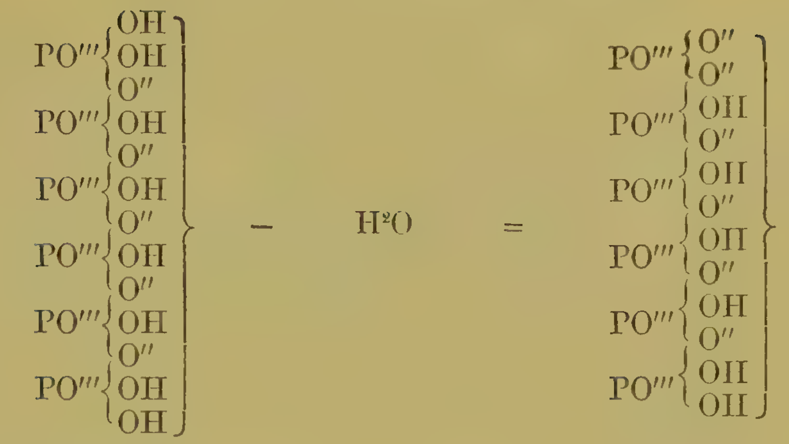


$$\left(\begin{array}{l}\mathrm{PO'''}\left\{\begin{array}{l}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{O}\end{array}\right.\\ \mathrm{PO'''}\left\{\begin{array}{l}\mathrm{OH}\\ \mathrm{OC^2H^3O}\end{array}\right.\end{array}\right);$$

that is to say, into pyrophosphoric acid in which one atom of hydrogen is replaced by acetyl ($C^2H^3O$). This acid forms well-defined salts. The hydrogen of pyrophosphoric acid is replaceable by fourths, which indicates that this acid contains at least four atoms. Its formula expressed with the old proportional numbers would therefore not be ($PH^2O^7$), but ($P^2H^2O^{14}$), which by atomic notation becomes ($P^2H^2O^7$).

Phosphoric anhydride dissolved in cold water produces, not phosphoric acid, but a first anhydride of this body acting as an acid and answering to the formula $\left(PO'''\left\{\begin{matrix}O''\\OH\end{matrix}\right.\right)$ or $\left(\left.\begin{matrix}(PO'''O)\\H\end{matrix}\right\}O\right)$. This compound is known under the name of metaphosphoric acid and only gives monometallic salts. It is phosphoric acid deprived of a molecule of water. Polymers of metaphosphoric acid also exist which are called bimetaphosphoric, trimetaphosphoric, tetrametaphosphoric, pentametaphosphoric, and hexametaphosphoric acids. These bodies appear to be the first anhydrides of condensed acids higher than pyrophosphoric acid, and as yet unknown. The following table shows these proportions :—

| | | | | |
|---|---|---|---|---|
| $PO'''\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right\}$ | $-$ | $H^2O$ | $=$ | $PO'''\left\{\begin{matrix}O''\\OH\end{matrix}\right\}$ |
| Phosphoric acid. | | Water. | | Metaphosphoric acid. |
| $\left.\begin{array}{rl}PO''' & OH\\ & OH\\ & O''\\ PO''' & OH\\ & OH\end{array}\right\}$ | $-$ | $H^2O$ | $=$ | $\begin{array}{rl}PO''' & \left\{\begin{matrix}O''\\O''\end{matrix}\right\}\\ PO''' & \left\{\begin{matrix}OH\\OH\end{matrix}\right\}\end{array}$ |
| Pyrophosphoric acid (diphosphoric) | | Water. | | Dimetaphosphoric acid. |
| $\left.\begin{array}{rl}PO''' & OH\\ & OH\\ & O''\\ PO''' & OH\\ & O''\\ PO''' & OH\\ & OH\end{array}\right\}$ | $-$ | $H^2O$ | $=$ | $\left.\begin{array}{rl}PO''' & O''\\ & O''\\ PO''' & OH\\ & O''\\ PO''' & OH\\ & OH\end{array}\right\}$ |
| Triphosphoric acid. (unknown). | | Water. | | Trimetaphosphoric acid. |
| $\left.\begin{array}{rl}PO''' & OH\\ & OH\\ & O''\\ PO''' & OH\\ & O''\\ PO''' & OH\\ & O''\\ PO''' & OH\\ & OH\end{array}\right\}$ | $-$ | $H^2O$ | $=$ | $\left.\begin{array}{rl}PO''' & O''\\ & O''\\ PO''' & OH\\ & O''\\ PO''' & OH\\ & O''\\ PO''' & OH\\ & OH\end{array}\right\}$ |
| Tetraphosphoric acid (unknown.) | | Water. | | Tetrametaphosphoric acid. |
| $\left.\begin{array}{rl}PO''' & OH\\ & OH\\ & O''\\ PO''' & OH\\ & O''\\ PO''' & OH\\ & O''\\ PO''' & OH\\ & O''\\ PO''' & OH\\ & OH\end{array}\right\}$ | $-$ | $H^2O$ | $=$ | $\left.\begin{array}{rl}PO''' & O''\\ & O''\\ PO''' & OH\\ & O''\\ PO''' & OH\\ & O''\\ PO''' & OH\\ & O''\\ PO''' & OH\\ & OH\end{array}\right\}$ |
| Pentaphosphoric acid (unknown). | | Water. | | Pentametaphosphoric acid. |



$$\left.\begin{array}{ll} & OH \\ PO''' & OH \\ & O'' \\ PO''' & OH \\ & O'' \\ PO''' & OH \\ & O'' \\ PO''' & OH \\ & O'' \\ PO''' & OH \\ & O'' \\ PO''' & OH \\ & OH \end{array}\right\} - H^2O = \left.\begin{array}{l} PO'''\begin{cases}O''\\O''\end{cases} \\ PO'''\begin{cases}OH\\O''\end{cases} \\ PO'''\begin{cases}OH\\O''\end{cases} \\ PO'''\begin{cases}OH\\O''\end{cases} \\ PO'''\begin{cases}OH\\O''\end{cases} \\ PO'''\begin{cases}OH\\OH\end{cases} \end{array}\right\}$$

Hexaphosphoric acid (unknown.) Water. Hexametaphosphoric acid.

Phosphoric, pyrophosphoric, and metaphosphoric acids may be easily distinguished by the help of albumen and nitrate of silver. Albumen is not coagulated either by phosphoric or pyrophosphoric acids, while metaphosphoric acid coagulates it. Nitrate of silver precipitates phosphoric acid yellow, and the meta- and pyrophosphoric acids white.

Their characteristics are shown in the following table :—

| | | |
|---|---|---|
| Metaphosphoric acid . . | Coagulates albumen . . | Gives a white precipitate with nitrate of silver. |
| Pyrophosphoric acid . . | Does not coagulate albumen. | Gives a white precipitate with nitrate of silver. |
| Phosphoric acid . . . . | Does not coagulate albumen. | Gives a yellow precipitate with nitrate of silver. |

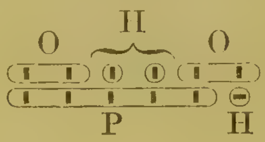
**Theory of the Acids of Phosphorus.**—The three simple acids of phosphorus all contain three atoms of hydrogen. But of these only one is replaceable by a metal in hypophosphorous acid, two in phosphorous acid, while all three can be so replaced in phosphoric acid.

To explain this fact we have merely to admit that in all these acids two of the five units of affinity of phosphorus are saturated by oxygen and that the three others are saturated :

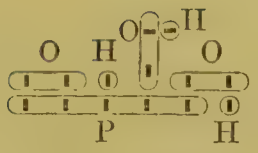
1st. In hypophosphorous acid, two by hydrogen and one by hydroxyl.

2nd. In phosphorous acid, two by hydroxyl and one only by hydrogen.

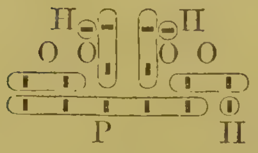
3rd. In phosphoric acid, all three by hydroxyl. The hydrogen united to the phosphorus by means of the oxygen would alone be replaceable by metals. The following figures show this constitution of the acids of phosphorus :—



= $(PH^3O^2)$ (hypophosphorous acid).



= $(PH^3O^3)$ (phosphorous acid).



= $(PH^3O^4)$ (phosphoric acid).

This theory of the acids of phosphorus was first propounded by M. Lieben.

### Combinations of Phosphorus with Sulphur.

The compounds $(P^4S)$, $(P^2S)$, $(P^2S^3)$, $(P^2S^5)$, and $(PS^6)$, exist; the first four correspond in composition to oxide of phosphorus, hypophosphorous, phosphorous, and phosphoric anhydrides. The fifth has no corresponding oxygenized compound.

These different bodies are prepared with difficulty from ordinary phosphorus, but may be easily procured from amorphous phosphorus.

The two first assume two particular allotropic states; they may present themselves either as liquids, volatile without decomposition, spontaneously inflammable, solidifiable at a low temperature, and decomposable by water; or as solid red bodies not affected by water, and not spontaneously inflammable.

Probably the liquid modification of these bodies contains the phosphorus in a crystallizable state, while the solid modification contains it in an amorphous condition.

## ARSENIC $\left.\begin{matrix}As^2\\As^2\end{matrix}\right\}$

Atomic weight = 75. Molecular weight = 300.

Arsenic is generally prepared by heating an arsenio-sulphide of iron (mispickel) with iron ore; the arsenic volatilizes and the sulphur remains in the state of sulphide of iron.

Very pure arsenic may also be obtained by passing vapours of arsenious anhydride over red-hot carbon, or by heating a mixture of lime and sulphide of arsenic.

Arsenic is solid at the ordinary temperature. Under the influence of heat it volatilizes without melting, unless the operation be conducted under pressure. The density of solid arsenic is 5·75 and its vapour density 10·39.

Arsenic is insoluble in water and crystallizable in rhombohedra by means of sublimation. It is very brilliant, and air soon tarnishes it, but steeping it in a solution of an alkaline hypochlorite restores its lustre by dissolving the slight layer of oxide which covered the surface.

Arsenic may be pulverized with the greatest ease. It is inodorous and tasteless. When thrown on hot charcoal it emits an alliaceous odour which does not pertain either to the vapours of arsenic or to those of arsenious anhydride, and which appears to show itself at the instant oxidation takes place.

Arsenic combines with oxygen at a very slightly elevated temperature, and it then burns with a pale-blue flame, producing arsenious anhydride (the white arsenic of commerce). It ignites spontaneously in an atmosphere of chlorine, forming chloride of arsenic.

Arsenicum is not poisonous of itself, but it becomes so under any influence that may cause its oxidation. Its oxides are very poisonous.

### COMBINATIONS OF ARSENICUM WITH MONATOMIC METALLOIDS.

Two arsenides of hydrogen are known: gaseous arseniuretted hydrogen ($AsH^3$), and the solid arsenide ($As^4H^2$), the latter analogous to solid phosphide of hydrogen.

**Arseniuretted Hydrogen** ($AsH^3$).—This body mixed with hydrogen is produced when nascent hydrogen is made to act on the oxy-acids of arsenic. It is prepared in a pure state by treating the arsenide of tin by hydrochloric acid:

$$\underset{\text{Arsenide of tin.}}{\left(As^2Sn^3\right)} + 6\underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = 3\underset{\text{Chloride of tin.}}{\left(\left.\begin{matrix}Sn\\Cl^2\end{matrix}\right\}\right)} + 2\underset{\text{Arseniuretted hydrogen.}}{\left(AsH^3\right)}$$

It is a colourless gas with a nauseous fetid odour, of a density of 2·695; it liquefies at about − 30° under the ordinary pressure of the atmosphere.

Heat decomposes arseniuretted hydrogen into arsenic and hydrogen, and electricity causes it to undergo a similar decomposition.

Arseniuretted hydrogen burns in air, forming water and arsenious anhydride; but if the oxygen be insufficient, as always occurs in the middle of the flame, water and arsenic are produced; therefore when the flame of the gas is cut by a cold body, a deposit of arsenicum is obtained.

Arseniuretted hydrogen, on contact with a solution of nitrate of silver, gives metallic silver, arsenic and nitric acids.

$$\underset{\text{Arseniuretted hydrogen.}}{\left(AsH^3\right)} + 8\underset{\text{Nitrate of silver.}}{\left(\left.\begin{matrix}NO^2\\Ag\end{matrix}\right\}O\right)} + 4\underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} =$$

$$8\underset{\text{Nitric acid.}}{\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)} + \underset{\text{Arsenic acid.}}{\left(\left.\begin{matrix}AsO'''\\H^3\end{matrix}\right\}O^3\right)} + 4\underset{\text{Silver.}}{\left(\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}\right)}$$

Arseniuretted hydrogen is analyzed in the same manner as phosphuretted hydrogen.

**Solid Arsenide of Hydrogen** ($As^4H^2$). (Synonym: *Hydride of Arsenic.*) —This compound is formed in several ways. M. Blondot recently discovered that it is formed every time that nascent hydrogen acts on the acids of arsenic in presence of nitric acid; the smallest quantity of this acid is sufficient to prevent the production of gaseous arseniuretted hydrogen and to determine that of the solid arsenide; nevertheless if organic substances be added to the mixture, the production of gaseous arseniuretted hydrogen alone takes place as in the absence of the nitric acid.

## Combinations of Arsenic with Chlorine, Bromine, and Iodine.

Chlorine, bromine, and iodine, combine directly with arsenic—the two first with production of light—and chloride, bromide, or iodide of arsenic is formed. The chloride of arsenic is liquid; it boils at 132° and freezes at − 29°; its formula is ($AsCl^3$).

The bromide is solid at the ordinary temperature; it melts at 20° and distils at 220°; its formula is ($AsBr^3$). The iodide is also solid, fusible and volatile, and answers to the formula ($AsI^3$); it is red, while the chloride and the bromide are colourless in the liquid and white in the solid state. These three bodies are decomposed by water into arsenious anhydride and hydrochloric, hydrobromic, or hydriodic acid.

$$\underset{\text{Bromide of arsenic.}}{2\left(AsBr^3\right)} + \underset{\text{Water.}}{3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Hydrobromic acid.}}{6\left(\left.\begin{matrix}H\\Br\end{matrix}\right\}\right)} + \underset{\text{Arsenious anhydride.}}{\left(As^2O^3\right)}$$

## Compounds of Arsenic with Oxygen.

Arsenic forms two compounds with oxygen: the arsenious anhydride ($As^2O^3$) and the arsenic anhydride ($As^2O^5$).

**Arsenious Anhydride** $\left(\left.\begin{matrix}AsO'''\\AsO'''\end{matrix}\right\}O\right)$.—This body may be prepared by burning arsenic in air, but it is generally obtained secondarily by roasting certain metallic arsenides.

Arsenious anhydride is dimorphous; sometimes it crystallizes in regular octahedra, sometimes in prisms with a rhombic base. When recently sublimed it assumes the aspect of a vitreous mass, but this left to itself becomes opaque, and this transformation proceeds from the surface to the centre.

Opaque arsenious anhydride has a density of 3·699, while the density of the vitreous anhydride is 3·738.

Arsenious anhydride is three times more soluble in water in the vitreous than in the opaque condition. At a low temperature water causes it to assume the opaque state, and the same effect is produced by trituration. Prolonged boiling, on the contrary, transforms the opaque into vitreous anhydride.

Arsenious anhydride is much more soluble in water acidulated with hydrochloric acid than in pure water. If such a solution be made, saturated while hot with vitreous anhydride and afterwards cooled, this body is deposited in an opaque state, and the formation of each crystal is accompanied by the emission of light.

Arsenious anhydride does not produce a corresponding acid by reacting with water; it reacts, on the contrary, with bases forming salts known as arsenites.

Arsenious anhydride is a virulent poison, but is nevertheless employed in medicine. It is a powerful febrifuge in intermittent fevers, which it will sometimes arrest when they have resisted the sulphate of quinine. Its composition has been determined by ascertaining the increase which a given weight of arsenic experiences when burnt in excess of oxygen.

The vapour density of arsenious anhydride is 13·85. It really corresponds to the formula ($As^4O^6$), and not to the formula ($As^2O^3$), which we have retained in order better to show the analogies of arsenic with nitrogen and phosphorus.

**Arsenic Anhydride** $\left( \left. \begin{matrix} \text{AsO}''' \\ \text{AsO}''' \end{matrix} \right\} \text{O}^3 \right)$.—Arsenic anhydride is obtained by transmitting a current of chlorine into an aqueous solution of arsenious anhydride, evaporating the solution to dryness, and heating the residue to a dull-red heat. Instead of the action of chlorine, that of aqua regia or boiling nitric acid may be substituted. Heated to bright redness, this compound divides into oxygen and arsenious anhydride, but a portion escapes decomposition and becomes volatilized.

If, instead of evaporating the above solution to dryness, it be only concentrated to the consistence of a syrup, and allowed to stand at a temperature below 15°, crystals of arsenic acid $\left( \text{AsO}''' \left\{ \begin{matrix} \text{OH} \\ \text{OH} \\ \text{OH} \end{matrix} \right. \right) + \text{aq.}$ are obtained, These crystals lose their water of crystallization at 100°.

If the temperature be raised to 180° it becomes transformed into a new acid, which by its composition appears to be analogous to pyrophosphoric acid, and to which we will give the formula
$$\left( \begin{array}{ll} & \text{OH} \\ \text{AsO}''' & \left\{ \text{OH} \right. \\ & \text{O} \\ \text{AsO}''' & \left\{ \text{OH} \right. \\ & \text{OH} \end{array} \right)$$

A saturated solution of this acid kept at 205° or 206° deposits crystals answering to the formula $\left(AsO'''\left\{\begin{matrix}O''\\OH\end{matrix}\right.\right)$, or to a multiple of this formula. It is meta-arsenic acid.

M. Maumené has recently questioned the analogies of the different acids of which we have just spoken with phosphoric, metaphosphoric, and pyrophosphoric acids. This chemist states that he has tried unsuccessfully to prepare meta- and pyroarseniates. If his experiments are to be relied on, the preceding bodies must therefore be regarded as the arsenic anhydride containing water of crystallization, and their formulæ must be $(As^2O^5,3aq)$; $(As^2O^5,2aq)$; $(As^2O^5,aq)$.

Nevertheless, the first formulæ appear the more probable, and I think that M. Maumené's experiments should be repeated.

### Combinations of Arsenic with Sulphur.

Five sulphides of arsenic are known; they are represented by the formulas:

$$(As^2S) - (As^2S^2) - (As^2S^3) - (As^2S^5) - (As^2S^{18}).$$

## ANTIMONY $\left.\begin{matrix}Sb^2\\Sb^2\end{matrix}\right\}$

Atomic weight = 122. Molecular weight = 488.

Antimony exists in nature in the state of sulphide. When the mineral has been melted and freed from its earthy impurities, it is called crude antimony. This body is roasted (that is to say, calcined in air) in order to partially transform it into an oxide, according to the equation:

$$\underset{\text{Sulphide of antimony.}}{2(Sb^2S^3)} + \underset{\text{Oxygen.}}{9\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\right)} = \underset{\text{Sulphurous anhydride.}}{6(SO^2)} + \underset{\text{Oxide of antimony.}}{2(Sb^2O^3)}$$

The roasted mineral is then heated with charcoal moistened with a very concentrated solution of carbonate of sodium. This salt transforms the remaining sulphide of antimony into oxide, and the carbon reduces the oxide to the state of free antimony:

$$\text{1st.}\quad \underset{\text{Sulphide of antimony.}}{\left(Sb^2S^3\right)} + \underset{\text{Carbonate of sodium.}}{3\left(\left.\begin{matrix}CO''\\Na^2\end{matrix}\right\}O^2\right)} = \underset{\text{Carbonic anhydride.}}{3\left(CO^2\right)} + \underset{\text{Sulphide of sodium.}}{3\left(\left.\begin{matrix}Na\\Na\end{matrix}\right\}S\right)} + \underset{\text{Oxide of antimony.}}{\left(Sb^2O^3\right)}$$

$$\text{2nd.}\quad \underset{\text{Oxide of antimony.}}{2(Sb^2O^3)} + \underset{\text{Carbon.}}{6C} = \underset{\text{Oxide of carbon.}}{6(CO)} + \underset{\text{Antimony.}}{\left(\left.\begin{matrix}Sb^2\\Sb^2\end{matrix}\right\}\right)}$$

To purify the antimony thus obtained, it is heated with an excess of nitric acid, which transforms the antimony into an insoluble oxide

($Sb^2O^4$), while the substances that were mixed with the metalloid pass to the state of soluble compounds. The oxide is well washed, dried, and finally reduced by charcoal.

Antimony is silver white; it possesses a metallic lustre and is brittle, so that it can be pulverized very easily.

The density of antimony is 6·702; it crystallizes in a form much resembling that of rhombohedra; it melts at 430°, and volatilizes at red heat. Exposed to the air at an ordinary temperature, it does not alter, but at red heat it burns, being transformed into oxide; when pulverized, it inflames spontaneously in an atmosphere of chlorine.

Antimony is dissolved with very great difficulty by hydrochloric acid, which property enables it to be separated from tin. Sulphuric acid, concentrated and boiling, dissolves it with disengagement of sulphurous anhydride and formation of sulphate of antimony. Nitric acid transforms it into an intermediate oxide. Aqua regia dissolves it, causing it to pass either to the state of protochloride or to that of perchloride, according to the preponderance of the antimony or of the aqua regia.

Like tin and zirconium, antimony forms an oxide which acts as a basic anhydride and reacts with acids, forming salts.

### COMBINATION OF ANTIMONY WITH HYDROGEN.

Antimoniuretted hydrogen has never been obtained in a pure state; it is always produced when nascent hydrogen is made to act on a soluble compound of antimony. It is decomposed by heat into antimony and hydrogen: in a word, its properties resemble those of arseniuretted hydrogen. Considering the numerous analogies which arsenic and antimony present in most of their compounds, it can scarcely be doubted that antimoniuretted hydrogen ought to be represented by the formula ($SbH^3$).

### COMBINATIONS OF ANTIMONY WITH CHLORINE, BROMINE, AND IODINE.

On causing dry chlorine to act on a great excess of antimony placed in a glass retort and gently heated, a terchloride is obtained of a butter-like consistence ($SbCl^3$). This chloride is decomposed by water, forming hydrochloric acid and an insoluble oxychloride ($SbClO$) known under the name of *powder of Algaroth.* After long-continued washings, this latter body is transformed into a hydrate ($SbO,OH$), which heat converts into an oxide ($Sb^2O^3$) with elimination of water. The terchloride of antimony is a caustic, used in medicine under the name of butter of antimony.*

In presence of an excess of chlorine, antimony forms a perchloride ($SbCl^5$), which water decomposes into hydrochloric and antimonic acids ($SbH^3O^4$), and which gives a chlorosulphide ($SbCl^3S$) when acted on by sulphuretted hydrogen.

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* The terchloride, being the first chloride of antimony, is also called protochloride.

Bromine and iodine combine similarly with antimony; its combinations with these bodies which correspond to the protochloride, are the only ones that have hitherto been examined.

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### COMBINATIONS OF ANTIMONY WITH OXYGEN.

Three compounds of antimony with oxygen are known; they are, the protoxide or teroxide ($Sb^2O^3$), the intermediate oxide ($Sb^2O^4$), and the antimonic anhydride ($Sb^2O^5$), to which the antimonic and meta-antimonic acids correspond.

**Protoxide of Antimony** ($Sb^2O^3$).—This body is prepared either by oxidizing antimony in air, or by precipitating the protochloride of this metalloid by a base, washing and drying the precipitate:

$$\underset{\text{Protochloride of antimony.}}{2\left(SbCl^3\right)} + \underset{\text{Hydrate of potassium.}}{6\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Chloride of potassium.}}{6\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)} + \underset{\text{Protoxide of antimony.}}{\left(Sb^2O^3\right)} + \underset{\text{Water.}}{3\left(H^2O\right)}$$

Before being dried, the formula of the precipitate is ($SbHO^2$). The precipitated oxide dissolves in alkaline bases unless the precipitation has been caused by ammonia. The oxide prepared by direct oxidation may crystallize in prisms or in regular octahedra; it is therefore dimorphous, like arsenious anhydride, to which its composition corresponds.

The protoxide of antimony is a basic anhydride. It dissolves in acids, forming salts, in which the hydrogen of the acids is replaced by the group (SbO), acting either as monovalent or as trivalent. Salts of antimony are generally decomposed by water, forming a sub-salt which precipitates, and a strongly acid salt which remains in solution. In these solutions hydrosulphuric acid causes an orange precipitate, which is soluble in the hydrosulphate of ammonium and in boiling hydrochloric acid. A sheet of tin or zinc introduced causes a deposit of free antimony, which is but slightly acted on by boiling hydrochloric acid.

It is a remarkable fact that no oxygenized salt of antimony answering to the formula $\left(\left.\begin{matrix}Sb'''\\R^3\end{matrix}\right\}O^3\right)$ is known; all are derived from the hydrate $\left(\left.\begin{matrix}SbO\\H\end{matrix}\right\}O\right)$ by the substitution of an acid radicle for the hydrogen it contains, or they are acid salts which contain the monovalent residue (SbO) of this hydrate.

**Antimonic Anhydride** $\left(\left.\begin{matrix}SbO'''\\SbO'''\end{matrix}\right\}O^3\right)$.—This body is obtained by dissolving antimony in aqua regia, evaporating to dryness, and calcining the residue at a dull red heat.

When antimony is treated by nitric acid with a little hydrochloric acid, and the white insoluble powder which is produced is not calcined, this has for formula $\left(SbO'''\left\{\begin{matrix}O\\OH\end{matrix}\right.\right)$. It is an acid analogous to metaphosphoric acid, and represents the first anhydride of an unknown acid, the formula of which would be $\left(SbO'''\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.\right)$

The acid $\left(SbO'''\left\{\begin{matrix}O''\\OH\end{matrix}\right.\right)$ is called antimonic acid. In presence of bases it exchanges H for a metal, and forms salts whose general formula is $\left(SbO'''\left\{\begin{matrix}O\\OM'\end{matrix}\right.\right)$.

On decomposing the perchloride of antimony by water, another acid is obtained which is analogous to pyrophosphoric acid; it is the metaantimonic acid of M. Fremy; its formula is $\left(\begin{array}{ll} & OH\\ SbO''' & OH\\ & O''\\ SbO''' & OH\\ & OH\end{array}\right)$; it can exchange 4 atoms of hydrogen for 4 atoms of metal; but on contact with water its neutral salts always decompose into free base and an acid salt, answering to the formula $\left(\begin{array}{ll} & OM'\\ SbO''' & OH\\ & O''\\ SbO''' & OH\\ & OM'\end{array}\right)$

The potassic salt which corresponds to this formula possesses the property of precipitating the salts of soda in the state of insoluble bimet-antimoniate.

When antimony is treated by nitrate of potassium at a high temperature, the antimoniate of potassium $\left(SbO'''\left\{\begin{matrix}O\\OK\end{matrix}\right.\right)$ is produced, which dissolves after some time in boiling water, and there remains an insoluble powder, whose formula is

$$\left(\begin{array}{ll} SbO''' & \left\{\begin{matrix}O''\\O''\end{matrix}\right.\\ SbO''' & \left\{\begin{matrix}OK\\O''\end{matrix}\right.\\ SbO''' & \{OK\\ SbO''' & \left\{\begin{matrix}O''\\O''\end{matrix}\right.\end{array}\right) = ((SbO''')^4K^2O^7).$$

This salt appears to correspond to an acid

$$\left(\begin{array}{ll} SbO''' & \left\{\begin{matrix}O''\\O''\end{matrix}\right.\\ SbO''' & \left\{\begin{matrix}OH\\O''\end{matrix}\right.\\ SbO''' & \{OH\\ SbO''' & \left\{\begin{matrix}O''\\O''\end{matrix}\right.\end{array}\right) = ((SbO''')^4H^2O^7),$$

which would be the second anhydride of an unknown acid

$$\left(\begin{array}{l} SbO''' \left\{\begin{array}{l} OH \\ OH \end{array}\right. \\ SbO''' \left\{\begin{array}{l} O'' \\ OH \end{array}\right. \\ SbO''' \left\{\begin{array}{l} O'' \\ OH \end{array}\right. \\ SbO''' \left\{\begin{array}{l} O'' \\ OH \\ OH \end{array}\right. \end{array}\right) = ((SbO''')^4H^6O^9).$$

It is evident that there are the closest analogies between the antimonic and the phosphoric acids.

**Intermediate Oxide of Antimony** ($Sb^2O^4$).—This body is obtained in the form of an insoluble white powder by roasting the sulphide of antimony until it ceases to absorb oxygen. This compound may be considered as the antimoniate of antimonyl $\left(SbO'''\left\{\begin{array}{l} O'' \\ SbO'^2 \end{array}\right.\right)$.

## COMBINATIONS OF ANTIMONY WITH SULPHUR.

Two sulphides of antimony are known, the tersulphide ($Sb^2S^3$), and the pentasulphide ($Sb^2S^5$). They are obtained by transmitting a current of sulphuretted hydrogen into the solution of the corresponding chlorides ($SbCl^3$) and ($SbCl^5$).

The tersulphide is also obtained by heating the requisite proportions of antimony and sulphur. Hydrogen reduces it under the influence of heat, forming hydrosulphuric acid and liberating antimony.

The pentasulphide gives up sulphur to sulphide of carbon, and may, therefore, be only a simple mixture. True sulpho-salts correspond to the two sulphides of antimony; and these sulphides are dissolved in the solution of alkaline sulphides, and may be regarded as acid anhydro-sulphides.

There exists a compound of sulphide and protoxide of antimony which has a certain degree of importance, because it is much used in medicine as an expectorant and sudorific, or as a sedative in parenchymatous inflammations. It is kermes mineral.

To prepare kermes, carbonate of sodium is made to react on sulphide of antimony, either by heating a mixture of these bodies to redness, or by boiling sulphide of antimony in a solution of carbonate of sodium. Even when the operation is conducted by the first method it is afterwards completed by boiling in water, which theoretically reduces these two processes to one. When the boiling has lasted long enough, the liquid is filtered while hot, and the kermes is deposited on cooling.

The following is the theory of this operation: by the reaction of one part of carbonate of sodium on one part of sulphide of antimony, oxide of antimony and sulphide of sodium are formed:

$$\underset{\text{Sulphide of antimony.}}{\left(Sb^2S^3\right)} + \underset{\text{Carbonate of sodium.}}{3\left(\left.\begin{matrix}CO''\\Na^2\end{matrix}\right\}O^2\right)} = \underset{\text{Carbonic anhydride.}}{3\left(CO^2\right)} + \underset{\text{Sulphide of sodium.}}{3\left(\left.\begin{matrix}Na\\Na\end{matrix}\right\}S\right)} + \underset{\text{Oxide of antimony.}}{\left(Sb^2O^3\right)}$$

The oxide of antimony remains dissolved by means of the carbonate of sodium not decomposed, and the unaltered sulphide of antimony is held in solution by means of the sulphide of sodium. But as oxide and sulphide of antimony dissolve in their respective solvents more readily when hot than when cold, both are deposited by the cooling of the liquid, and constitute kermes.

The cooled liquid still contains oxide and sulphide of antimony in solution. If it be treated by hydrochloric acid, the latter will decompose the carbonate and sulphide of sodium, and precipitate an additional quantity of the oxide and sulphide of antimony. The oxide reacts on the hydrosulphuric acid arising from the decomposition of sulphide of sodium and becomes wholly transformed into sulphide; so that in this second operation only hydrated sulphide of antimony is obtained. This sulphide even contains a little polysulphide, which arises from the liberation of a small quantity of sulphur by the hydrochloric acid at the expense of the sodic polysulphides formed by the action of air on the monosulphide of sodium:

$$\underset{\text{Sulphide of sodium.}}{3(Na^2S)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} = \underset{\text{Oxide of sodium.}}{2(Na^2O)} + \underset{\text{Trisulphide of sodium.}}{(Na^2S^3)}$$

The mixture of trisulphide and hydrated pentasulphide is known as the golden sulphide of antimony.

On roasting crude sulphide of antimony, oxysulphides are obtained, known as glass of antimony, liver of antimony, crocus metallorum, etc.

## BISMUTH $\left.\begin{matrix}Bi^2\\Bi^2\end{matrix}\right\}$

Atomic weight = 210. Probable molecular weight = 840.

Bismuth exists in the native state; its extraction consists in simple fusion to free it from earthy impurities. In order to render it entirely pure, it is dissolved in nitric acid, and a large quantity of water is added to the solution: the bismuth is precipitated in the state of subnitrate, while all the metals with which it was combined remain in solution. The precipitate is washed, dried, and calcined in a crucible with charcoal. On cooling, very pure bismuth collects at the bottom of the crucible.

Bismuth has a reddish-white colour; it is hard and so brittle that it can be pulverized very easily. It melts at 267°, and by means of fusion crystallizes in large pyramids formed by superposed cubic crystals. These crystals are generally covered with a slight layer of oxide, and present the appearance of coloured rings. At a very high temperature bismuth volatilizes. Its density is 9·9 It does not oxidize in dry air; if the air be moist, it tarnishes a little, and under the simultaneous influence of air and heat it rapidly becomes oxidized.

Chlorine easily combines with bismuth. Dilute hydrochloric and hydrosulphuric acids do not act on it: hot concentrated sulphuric acid dissolves it, disengaging sulphurous anhydride.

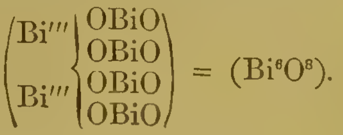
Cold nitric acid dissolves bismuth, forming trisnitrate.

All soluble salts, in which bismuth acts as the positive element, are decomposed by water with the formation of a basic salt which is precipitated, and the liberation of a certain quantity of acid which preserves a portion of neutral salt undecomposed.

Salts of bismuth are neither precipitated by hydrochloric nor by sulphuric acid. Ammonia causes the formation of a white precipitate insoluble in excess of ammonia. Hydrosulphuric acid gives a black precipitate, insoluble in sulphide of ammonium, and soluble in boiling nitric acid.

Chlorine combines with bismuth, forming a chloride whose formula is ($BiCl^3$), and which is soluble in water acidulated with hydrochloric acid. A larger quantity of water decomposes this solution, and precipitates an oxychloride (BiOCl), which, before being dried, is represented by the formula 2(BiOCl)+aq. By calcining the subnitrate of bismuth prepared as above, an oxide is obtained whose formula is ($Bi^2O^3$), and which is a basic anhydride. The hydrate ($BiHO^2$) may also be obtained by precipitating a soluble salt of bismuth by potash. This hydrate is the first anhydride of the unknown hydrate ($BiH^3O^3$).

On the preceding hydrate being mixed with a very concentrated solution of potash, and the mixture submitted to the action of a current of chlorine, a blood-red substance is separated, which, treated by acids, gives bismuthic acid. This acid is transformed by the action of heat into bismuthic anhydride ($Bi^2O^5$). It is not known to which of the phosphoric acids the normal bismuthic acid corresponds. A rather strong heat transforms bismuthic anhydride into an intermediate oxide ($Bi^3O^4$), which may be regarded as a pyrobismuthate of bismuthyl if its formula be doubled. We then have



$$\left(\begin{matrix} Bi''' \\ \\ Bi''' \end{matrix}\left\{\begin{matrix} OBiO \\ OBiO \\ OBiO \\ OBiO \end{matrix}\right.\right) = (Bi^6O^8).$$

By melting bismuth with sulphur, a sulphide ($Bi^2S^3$) is obtained, which may also be prepared in a state of hydrate by transmitting a current of hydrosulphuric acid into the solution of a salt of bismuth.

HOOL OF
DICINE

## URANIUM $\left.\begin{matrix}U^2\\U^2\end{matrix}\right\}$

Atomic weight = 120. Probable molecular weight = 480.

Uranium is obtained in the free state by decomposing its protochloride by potassium with the aid of heat. The uranium remains in the form of a dark-grey powder, partly agglomerated.

Heated to white redness in a crucible with chloride of sodium, uranium becomes yellowish white, hard, and somewhat malleable. Its density is then 18·4; it becomes yellower on contact with air. Powdered uranium burns in chlorine, and unites with sulphur at the boiling point of this body, with the production of light. Acids dissolve it, disengaging hydrogen, and the solutions are green when the acid does not act as an oxidant.

Uranium burns in air with a bright incandescence.

It forms several compounds with oxygen; two are especially interesting: the protoxide (UO), and the sesquioxide ($U^2O^3$). Both really, like the sesquioxide of antimony, act as basic anhydrides. The sesquioxide also acts as an acid anhydride; to each of these two oxides, therefore, a series of salts corresponds, and the uranates correspond to the sesquioxide.

We will only here mention the sesquioxide, which alone has a theoretic importance.

**Sesquioxide of Uranium** ($U^2O^3$).—There is a mineral, the pitchblende of Bohemia, which is chiefly composed of oxidized uranium. If this mineral be heated with nitric acid, a yellow solution is obtained containing nitrate of uranium. This solution evaporated to dryness leaves a residue, which is submitted to the action of ether; this liquid dissolves the nitrate of uranium, and leaves the other substances. The ether is evaporated at the ordinary temperature, and thus the nitrate of uranium is obtained pure. On calcining this salt at 250° it is transformed into sesquioxide of uranium ($U^2O^3$).

By evaporating to dryness an alcoholic solution of uranic nitrate, and washing with water the residue of the strong reaction which is manifested at the end of the operation, M. Malaguti has obtained an uranic hydrate $\left(\left.\begin{matrix}UO\\H\end{matrix}\right\}O\right)$. This hydrate is the first anhydride of the unknown normal hydrate $\left(\left.\begin{matrix}U'''\\H^3\end{matrix}\right\}O^3\right)$.

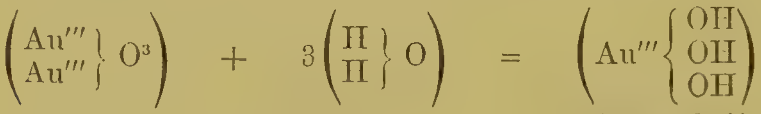
Uranic salts are all derived from this first anhydride by the substitution of an acid radicle for H. Their general formula is, therefore, $\left(\left.\begin{matrix}UO\\R\end{matrix}\right\}O\right)$. None are known derived from the normal hydrate $\left(\left.\begin{matrix}U'''\\H^3\end{matrix}\right\}O^3\right)$, and which would have the formula $\left(\left.\begin{matrix}U'''\\R^3\end{matrix}\right\}O^3\right)$.

This fact, analogous to that we have already observed in the case of antimony, is not surprising. We know that to all basic or acid hydrates containing more than two atoms of hydrogen, anhydrides acting as either acids or bases, and in consequence capable of forming salts, correspond. Now, according to the bodies, sometimes it is the grouping of the normal hydrate which is the most stable; in this case the principal salts present this grouping, and if some are obtained that are derived from anhydrides they are instable, and always have a tendency to return to the grouping of the normal hydrate. Sometimes, on the contrary, it is the grouping of the anhydride which has the greatest stability: the salts then present this grouping, and if sometimes some are obtained derived from the normal hydrate, they always have a tendency to return to the type of the anhydride. It may also happen that the bodies belonging to the type of the normal hydrate are so unstable that none of them can be prepared.

We have an example of the first order of these facts in phosphoric acid and its salts, and of the second order in uranic and antimonious salts.

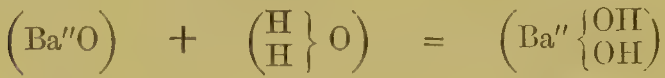
Formerly, when our present ideas on atomicity had not been formed, the formation of salts was accounted for in a totally different manner. It was believed that they consisted of two simple or compound principles endowed with opposite electric polarity, and capable of being saturated reciprocally. In oxygenized salts, for instance, the existence was admitted of two separate oxygenized groups, one of which took the name of base, and the other that of acid. This theory is known as the binary theory. According to it, the sulphate of potassium $\left(\left.\begin{matrix}SO^{2''}\\ K^2\end{matrix}\right\} O^2\right)$, for instance, would be written $(K^2O),(SO^3)$; the existence of two groups already formed was supposed: one of these $(K^2O)$ (basic anhydride) received the name of base, while the other $(SO^3)$ (acid anhydride) was called acid. Our normal acids and bases were combinations of an acid or base with water. Sulphuric acid was written $(SO^3),(H^2O)$, and potash $(K^2O),(H^2O)$. Often this could only be done by doubling the formulas, which more exact knowledge of molecular weights has shown us to be more simple, or by accepting as *equivalents* numbers half the value of our actual atomic weights. Thus nitric acid $(NHO^3)$ could only be written as $N^2O^5,H^2O = (N^2H^2O^6)$, and then the formula was double the true one; or $NO^5,HO$, and then $O$ was made $= 8$, while in reality the atomic weight of oxygen is 16. Among the different reasons which caused chemists to abandon the binary theory, this is the strongest. This theory, in fact, is in disaccordance either with our molecular or else with our atomic weights.

When we have a basic anhydride containing several atoms of oxygen, we now say that to this anhydride a perhydrate corresponds, and often anhydrides containing still more hydrogen; we call the first hydrates, and the salts derived hydrates and normal salts, to distinguish these bodies from all those which present the grouping of anhydrides. Moreover, we know that when the simple body combined with oxygen has an uneven atomicity, the hydrate is formed by double decomposition, and contains as much hydroxyl as the oxide contained oxygen; while, if the atomicity be even, the hydrate is formed by addition, and contains twice as many atoms of hydroxyl as the oxide contained oxygen.



$$\left(\left.\begin{matrix}Au''' \\ Au'''\end{matrix}\right\} O^3\right) + 3\left(\left.\begin{matrix}H \\ H\end{matrix}\right\} O\right) = \left(Au'''\left\{\begin{matrix}OH \\ OH \\ OH\end{matrix}\right.\right)$$

Oxide of gold. Water. Perhydrate of gold.



$$\left(Ba''O\right) + \left(\left.\begin{matrix}H \\ H\end{matrix}\right\} O\right) = \left(Ba''\left\{\begin{matrix}OH \\ OH\end{matrix}\right.\right)$$

Oxide of barium. Water. Hydrate of barium.

Now, as normal salts arise by the substitution of an acid radicle for the typical hydrogen of normal bases, we see that there is a relation between the number of atoms of oxygen which a basic oxide contains, and the number of acid radicles which form part of the normal neutral salts derived from these oxides.

Thus, in the case of oxides containing elements of uneven atomicity, the normal neutral salts ought to contain as many times the radicle of a monatomic acid as these acids contain oxygen. They ought to contain a double number in the case of basic oxides containing elements of even atomicity.

$(K^2O)$

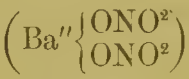
Potassic anhydride.

$(KONO^2)$

Potassic nitrate.

$(Ba''O)$

Barytic anhydride.



$$\left(Ba''\left\{\begin{matrix}ONO^2 \\ ONO^2\end{matrix}\right.\right)$$

Barytic nitrate.

According to the binary theory, this difference between the constitution of salts containing elements of even, and of those containing elements of uneven, atomicity did not exist. Atomicity not being understood, the first was doubled, or the second divided, and all became alike. Thus the salts we have taken as examples were considered either as:

$(K^2O)$

Oxide of potassium.

$(K^2O,N^2O^5)$

Nitrate of potash.

$(BaO)$

Oxide of barium.

$(BaO,N^2O^5)$

Nitrate of baryta.

or,

$(KO)$

Oxide of potassium.

$(KO,NO^5)$

Nitrate of potash.

$(BaO)$

Oxide of barium.

$(BaO,NO^5)$

Nitrate of baryta.

making in the second case $O = 8$ and $Ba = 68 \cdot 5$, instead of $O = 16$ and $Ba = 137$.

As is seen by these binary formulæ, the quantity of acid contained in a normal neutral salt was always equal to the number of atoms of oxygen contained in the base; thence this law of Richter:

"In neutral salts (normal neutral)* there is a constant relation between the acid and the oxygen of the base."

Which law Berzelius thus expressed:—"For the same species of neutral salts, there is a constant relation between the oxygen of the acid and the oxygen of the base."

Thus the nitrate of potash being $(KO,NO^5)$, the proportion between the oxygen of the base and that of the acid is 1 : 5; this same relation ought to exist between all neutral nitrates; if the base contain $O^2$, the acid ought to contain $O^{10}$; that is to say, that this salt ought to contain twice $NO^5$. If the base contain $O^3$, the salt ought to contain $3(NO^5)$, and so on. Thus, for example, the neutral nitrate of potash being $(KO,NO^5)$, the neutral pernitrate of iron was $(Fe^2O^3,3NO^5)$, and would have been $(Fe^4O^6,6NO^5)$, if to the sesquioxide of iron an equivalent equal to its molecular weight, which is 160, had been given, instead of the equivalent of 80.

The oxides of antimony and uranium, not conforming to the theory, were regarded as exceptions. These oxides containing $O^3$ ought, according to Richter's law, to unite with three equivalents of any acid to form neutral salts, while in reality they only unite to a single equivalent of acid.

To explain this anomaly, M. Peligot states that, in the sesquioxide of uranium $(U^2O^3)$†, the three equivalents of oxygen are not in the same state; two forming with uranium the compound radicle $(U^2O^2)$, and the other being combined with this radicle as it is with metals in the other oxides, the hydrate of uranium and its salts then became $(U^2O^2O,HO)$ and $(U^2O^2O,A)$, (A being any acid whatsoever). The normal proportion thus being established, this proportion ought to exist, not between the oxygen of the acid and the whole of the oxygen of the base, but between the oxygen of the acid and the fundamental oxygen of the base; that is to say, the oxygen whose presence gives its basic properties to the body.

With the atomic weight of uranium $U = 120$ and of oxygen $O = 16$, the radicle $(U^2O^2)$ becomes $(UO)$; we can therefore use M. Peligot's theory in our actual formulas, and inquire whether $(UO)$ is the radicle which exists in uranic salts.

Its presence, in fact, cannot be doubted, and we have expressed this idea when we said that these salts are derived from the first anhydride of the unknown normal hydrate. The anhydrides are formed by the substitution of O for $(OH^2)$ in a hydrate. If therefore the normal hydrate is $U'''\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.$, the first anhydride will be $U'''\left\{\begin{matrix}O''\\OH\end{matrix}\right.$, which formula may also be written $\left.\begin{matrix}UO'\\H\end{matrix}\right\}O$, to show that the typical hydrogen is there united to the uranyl (UO′) by the medium of the oxygen.

---

* That is, derived from a normal or saturated hydrate.

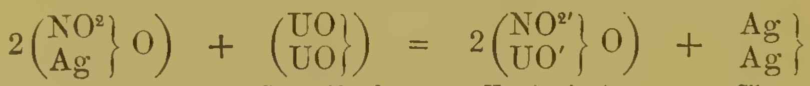
† $U = 60$, $O = 8$.

The grouping of the hydrate $\left(\left.\begin{matrix}UO\\H\end{matrix}\right\}O\right)$ is so stable that even the chloride corresponds to it. Thus on submitting the sesquioxide of uranium to the action of chlorine, we do not obtain the chloride $\left(U'''\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right.\right) = (U'''Cl^3)$, it is the oxychloride $\left(U'''\left\{\begin{matrix}O''\\Cl\end{matrix}\right.\right) = (UOCl)$ that is produced.

The several theoretical considerations we have just stated on the subject of uranium show how our present theories are more enlarged than former ones, since such facts are now considered as ordinary and normal which were formerly regarded as exceptions.

The sesquioxide of uranium is a bright yellow colour; strongly heated it loses part of its oxygen, and is transformed into a green oxide ($U^3O^4$). The sesquioxide easily dissolves in acids, forming yellow salts, and in alkaline solutions forming uranates, in which uranyl acts as an acid radicle. If it be mixed with carbon, and the mixture heated in a current of hydrogen, protoxide of uranium (UO), or rather ($U^2O^2$), is formed; in a current of chlorine the same mixture forms chloride ($UCl^2$), or rather ($U^2Cl^4$).

The protoxide placed in a solution of nitrate of silver gives a deposit of metallic silver and an uranic salt, in the same manner as a sheet of zinc would.



$$2\left(\left.\begin{matrix}NO^2\\Ag\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}UO\\UO\end{matrix}\right\}\right) = 2\left(\left.\begin{matrix}NO^{2\prime}\\UO'\end{matrix}\right\}O\right) + \left.\begin{matrix}Ag\\Ag\end{matrix}\right\}$$

Nitrate of silver. Protoxide of uranium. Uranic nitrate. Silver.

**Distinctive Characteristics of Salts of Uranium.**—The sub-salts (salts derived from the protoxide), such as protochloride ($U^2Cl^4$), are green; with caustic alkalies and ammonia they give a dark-brown gelatinous precipitate, which exposure to the air turns yellow by causing it to pass to the state of perhydrate.

Uranic salts (salts derived from the hydrate $\left(\left.\begin{matrix}UO\\H\end{matrix}\right\}O\right)$) are yellow; alkalies form in their solutions a yellow precipitate, soluble in an excess of the reagent.

Their alcoholic solutions exposed to the sun turn green, because they are reduced to sub-salts by losing oxygen.

## GENERAL REMARKS ON THE PENTATOMIC METALLOIDS.

The fundamental character of metalloids of this class is that they are pentatomic; they can unite with three or five monatomic atoms, forming compounds belonging to the two types $(R'''X^3)$ and $(R^vX^5)$.

It is remarkable that when a single monatomic radicle enters into combination with one of these bodies, the compound has a great tendency to assume the grouping $(RX^3)$, while when two different radicles intervene at the same time, the group $(RX^5)$ is the one that usually forms.

Bismuth and uranium are exceptions to this; they never form compounds corresponding to the formula $(RX^5)$. Nevertheless, if we consider that, commencing from nitrogen, the stability of the compounds of which we speak progressively decreases; if we consider moreover, that the combinations of bismuth and uranium with oxygen have the strictest analogy to the oxygenized combinations of antimony, we are obliged to admit that bismuth and uranium belong to the group of pentatomic metalloids, and that if their compounds answering to the formula $(RX^5)$ are not known, it is probably because they are too unstable to have been hitherto prepared.

Those of these metalloids which combine with hydrogen give compounds whose formula is $(RH^3)$. When the radicle R is nitrogen the compound eagerly combines with acids to pass to the grouping $(RX^5)$.

$$\underset{\text{Ammonia.}}{(NH^3)} + \underset{\text{Hydrochloric acid.}}{(HCl)} = \underset{\text{Chloride of ammonium.}}{(NH^4Cl)}$$

If the radicle R be phosphorus, the preceding reaction is only possible with hydrobromic and hydriodic acids, and even then the compounds formed are unstable.

Arseniuretted hydrogen and antimoniuretted hydrogen never unite either with hydracids nor with ox-acids. It is only when their hydrogen has been replaced by organic radicles that the group can be completed by the fixing of two new monatomic radicles.

We know that polyatomic radicles are capable of accumulating in the molecules, losing a fraction of their capacity for saturation equal to $2n - 2$, calling $n$ the number of atoms accumulated in one molecule. We also know that every compound which contains monatomic radicles may lose, successively, one, two, three . . . . . $n$ molecules of these latter, forming non-saturated bodies. According to this principle, a member of this class ought to be able to form, with monatomic radicles, the following compounds:

$RX^5 - RX^3 - RX$

$R^2X^8 - R^2X^6 - R^2X^4 - R^2X^2$

$R^3X^{11} - R^3X^9 - R^3X^7 - R^3X^5 - R^3X^3 - R^3X$

$R^4X^{14} - R^4X^{12} - R^4X^{10} - R^4X^8 - R^4X^6 - R^4X^4 - R^4X^2.$

We know very little concerning these products of condensation; nevertheless, there are two compounds of phosphorus and one of arsenic which evidently correspond to two of these formulæ. These are liquid phosphuretted hydrogen ($P^2H^4$), solid phosphuretted hydrogen ($P^4H^2$), and solid arsenide of hydrogen ($As^4H^2$).

Pentatomic metalloids can also unite with oxygen and with biatomic radicles in general. These latter radicles having the faculty of accumulating indefinitely, the quantity of their compounds possible is innumerable. Nevertheless, as the addition of any number of atoms of a radicle of even atomicity to one of these metalloids can only give one compound radicle of uneven atomicity, and as these radicles cannot exist in a free state, oxygen and its congeners ought only to combine with bodies of the nitrogen family on condition that the compound formed contain two atoms of the pentatomic metalloid (we speak of compounds capable of isolation, and not of radicles that can only act in combinations). But there are two exceptions to this rule: that of the protoxide of nitrogen, whose formula is ($NO$) and not ($N^2O^2$), and that of the hyponitride, whose formula is ($NO^2$) and not ($N^2O^4$).

## APPENDIX TO THE METALLOIDS.

**Atmospheric Air.**—The qualitative composition of atmospheric air was determined for the first time by Lavoisier, by means of the following experiment.

Lavoisier took a globe B (fig. 29), with a very long neck curved twice; the globe contained mercury, and the free end of the neck was passed under a bell-glass full of air E, placed over a bath of mercury D. The air contained in the globe could communicate freely with that contained in the bell-glass.

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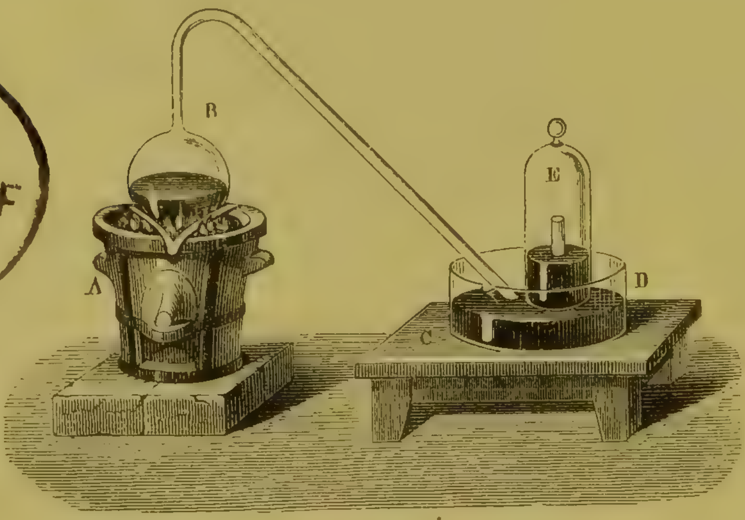

Fig. 29.

The apparatus being thus disposed, Lavoisier heated the globe for twelve days at a temperature about that of the boiling point of mercury. He observed, 1st, that the mercury in the globe became covered with a red layer: and, 2nd, that the volume of air in the bell-glass diminished.

After twelve days, the gaseous volume no longer diminishing and the red layer no longer appearing to increase, Lavoisier arrested the operation. He then recognized that the gas contained in the bell-glass possessed the properties we have described as belonging to nitrogen. He collected, on the other hand, the red layer produced, and heated it strongly in a small tube closed at one end. The mercury was re-formed, and a gas was disengaged in which Lavoisier recognised the properties we have described as belonging to oxygen.

This experiment showed that air is composed of two gases, to which Lavoisier gave the names which they still retain; but it could do nothing towards fixing its quantitative composition. Succeeding experimenters endeavoured to do this, and numerous processes have been successively employed.

Analysis of Air by Phosphorus.—A small graduated bell-glass containing a measured quantity of air is placed over a bath of mercury (fig. 30). A ball of phosphorus supported by a wire is introduced into the bell-glass, and the apparatus is left alone until the gaseous volume no longer diminishes, which sometimes requires a rather long time. Finally, it is shaken a little to precipitate the phosphorus vapour, and the remaining volume, which is nitrogen, is measured. Instead of this process another method may be employed, which consists in heating a piece of phosphorus in a curved bell-glass (fig. 31) by a small spirit lamp. The combination of the oxygen and phosphorus is then very rapid. The operation should be conducted in a vessel full of water, in order that the acids arising from the oxidization of the phosphorus may be dissolved.

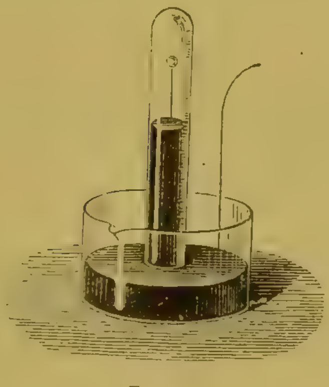

Fig. 30.

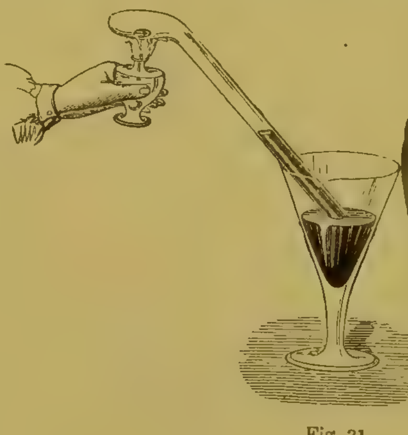

Fig. 31.

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In whatever way we operate, we find that $100^{cc}$ of air leave a residue of $79^{cc}$, which gives $21^{cc}$ for the oxygen consumed.

Analysis of Air by Copper and Acids.—In presence of acids copper absorbs oxygen. If therefore a sheet of copper moistened with sulphuric acid be placed in a test tube containing a known volume of air, after a certain time the metal will have absorbed all the oxygen, and there will only remain in the tube pure nitrogen, which may be measured.

PROCESS BY PYROGALLIC ACID AND POTASH.—In contact with potash, pyrogallic acid absorbs oxygen. It is therefore only necessary to shake a tube full of air placed over mercury, after having introduced successively, by means of a small curved tube, pyrogallic acid and potash, and to measure the gas which remains after absorption. This gas consists of pure nitrogen, and the amount of oxygen is determined by the difference.

EUDIOMETRIC PROCESS.—A measured volume of atmospheric air $V$, and an equal one of hydrogen $V'$, are introduced into a eudiometer, and the amount of the given volume of the mixture is $V + V'$.

An electric spark is transmitted, and after the explosion the gas which remains is measured; let its volume be $V''$; $V + V' - V''$ represents the gas that has disappeared by the combustion. This gas has passed into the state of water, and the mixture of hydrogen and oxygen capable of being entirely transformed into water contains $\frac{1}{3}$ of oxygen. Therefore the volume $V$ of air contained $\frac{V + V' - V''}{3}$ of oxygen, and $V - \frac{V + V' - V''}{3}$ of nitrogen.

We find by this process, as by the analysis made by means of phosphorus, that air contains in a hundred parts:

| | |
|---|---|
| Oxygen . . . . | 21 volumes. |
| Nitrogen . . . . | 79 „ |

MM. DUMAS AND BOUSSINGAULT'S PROCESS.—In this method the constituent elements of air are proportioned by weight. Moreover, if necessary, not only the oxygen and nitrogen, but also the carbonic anhydride and the vapour of water which air contains, may be determined in the same experiment.

The apparatus is composed (fig. 32), 1st, of a large globe A, furnished at the upper part with a brass neck having an air-tight stopcock R, above which is fastened a bent glass tube B. 2nd. This tube communicates through a brass stopcock R′ fitted, by means of india-rubber, with another larger tube of porcelain placed on a grating of sheet iron C. 3rd. The porcelain tube is closed at the other extremity by a stopcock R″, by means of which it communicates with a series of U and Liebig's tubes full either of solution of potash or sulphuric acid, or of pumice-stone moistened with sulphuric acid or potash, or of solid potash, for the purpose of absorbing the carbonic anhydride and watery vapour. Before the operation the globe A is exhausted, after which its weight $p$ is ascertained. The porcelain tube is filled with copper filings, the air exhausted, and its weight $p'$ also ascertained; finally, if we wish to ascertain the proportions of the water and carbonic anhydride, the whole of the potash and sulphuric acid apparatus is likewise weighed.

This done, the apparatus is mounted, the tube containing the metallic copper is heated to redness, then the tap R″ is opened, care being taken to allow the air to enter only slowly. When this tube is full of gas, which is known by no more air bubbles passing into the bulb-tubes, the tap R′ is opened. The air then rushes into the globe, and when it ceases to pass, the taps R, R′, and R″ are closed and the apparatus is dismounted.

The air, on passing over the red-hot copper, leaves its oxygen with the metal, so that the porcelain tube at the end of the operation contains all the oxygen of the decomposed air. The nitrogen fills both this tube and the globe A.

The globe A full of nitrogen is weighed; let P be its weight; $P - p$ represents the weight of nitrogen it contains.

The porcelain tube full of nitrogen is also weighed; let $P'$ be its weight. Then it is exhausted and its weight $P''$ again determined. $P' - P''$ indicates the quantity of nitrogen which this tube contained, and in consequence the total quantity of nitrogen is: $P - p + P' - P''$.

On the other hand, $P'' - p'$ represents the weight of the oxygen fixed by the copper.

Finally, let us represent by Q and by $Q'$ the weights of the water and the carbonic anhydride condensed in the tubes placed in the first part of the apparatus.

The weight of the air decomposed being necessarily equal to the amount of that of the different elements constituting it, is therefore:

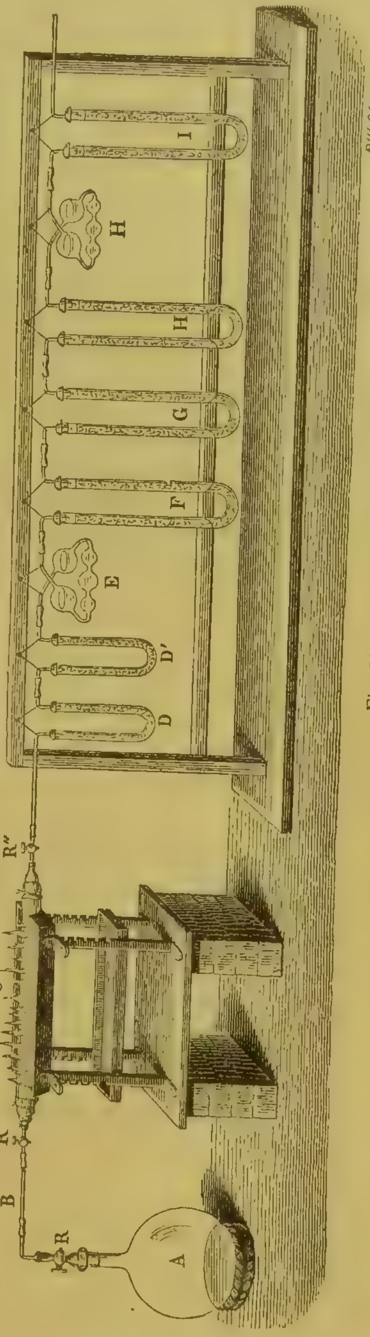

Fig. 32.

$$P - p + P' - P'' + P'' - p' + Q + Q'.$$

Thus the weights of the nitrogen, oxygen, carbonic anhydride, and watery vapour contained in a given weight of air are determined.

These numbers have only to be transformed into volumes by taking as bases the densities of oxygen and nitrogen.

MM. Dumas and Boussingault have in this manner demonstrated that air contains in weight:

| | |
|---|---|
| Oxygen . . . . . . | 23 |
| Nitrogen . . . . . | 77 |

and in volumes:

| | |
|---|---|
| Oxygen . . . . . . | 20·8 |
| Nitrogen. . . . . | 79·2 |

Carbonic anhydride and vapour of water enter into air in variable proportions. This fluid contains a mean of from 3 to 6 parts in a thousand of the first of these bodies, and of the second, from 6 to 9 in a thousand.

When, after freeing air from all the carbonic anhydride it contains, it is mixed with hydrogen, and submitted to the electric spark, it is stated that a very small quantity of carbonic anhydride is formed, sufficient to give a precipitate in lime-water. This experiment shows that, besides carbonic anhydride, air contains another combustible carbonized substance whose nature is unknown. Traces of ammonia are also found in air, and M. Barral has in addition discovered the presence of a phosphorized substance.

After having shown the invariability of the proportion existing between the oxygen and nitrogen of the air, there remains to be considered whether these bodies are chemically combined, or simply mixed.

Air must be considered as merely a mixture of the gases without combination for the following reasons:

1st. In the combinations of gases a simple relation is always observed between the volumes of the combined gases and that of the compound formed. Moreover, the combination is constantly accompanied by contraction, unless the two gases which unite do not enter into combination in equal volumes. There is no simple relation between the volumes of nitrogen and oxygen contained in air, and the sum of their volumes represents exactly the volume of the air without any contraction.

2nd. When quantities of nitrogen and oxygen equal to those constituting air are mixed, air is obtained possessing all its properties. Nevertheless the most exact thermometers cannot show any elevation of temperature, and the most delicate electroscopes show no development of electricity, while combination is always accompanied by both.

3rd. In air oxygen and nitrogen retain their own solubilities, and as oxygen is more soluble than nitrogen, air taken from water contains more oxygen than the ordinary atmosphere. This phenomenon could not exist if air were a combination, for then the two gases which constitute it would have each lost its own, to acquire a common solubility.

4th. The refracting power of compound gases is always greater or less than the sum of that of their elements. Air, on the contrary, has a refracting power equal to the amount of that of its elements.

Air owes the invariability of its constitution chiefly to its enormous mass, which causes its variations to be scarcely appreciable. It also owes it partly to the action of vegetation, which decomposes carbonic anhydride under the influence of solar radiation and restores the oxygen to the atmosphere. Nevertheless the quantity of carbonic anhydride produced appears to be larger than that of the oxygen given, so that the invariability observed may be only apparent, and be owing to the comparatively short time which has elapsed since the composition of air has been known.

It is probable that before the appearance of animals on the globe, when vegetation alone existed, the composition of the air was modified inversely, that is to say, the proportion of carbonic anhydride decreased and that of oxygen augmented. Is it not possible that, after an immense period, air may become unfit for the respiration of animals, so that again vegetation alone will exist on the globe for a series of centuries, until it shall a second time render the air fit for animals to breathe?

It is even possible that, before the distant epoch when probably all life will disappear from the surface of the earth, many similar periods may succeed each other.

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# METALS.

## CLASSIFICATION.

Up to the present time the classification of metals has been quite artificial ; it was created by M. Thenard, and is based on the action which heat exercises on metallic oxides, and on the property metals have of decomposing water at more or less elevated temperatures, or of not decomposing it at all.

Metals are first arranged in two sections ; the first containing those whose oxides cannot be decomposed by heat alone, and the second, those whose oxides are decomposed by heat.

### First Section.

**Metals whose Oxides cannot be decomposed by heat alone.**

This section contains the five following classes :

#### 1st Class.—*Metals decomposing cold water.*

Potassium.
Sodium.
Lithium.
Barium.
Strontium.
Calcium.

The three first of these have been called alkaline metals, and the three last, metals of the alkaline-earths. To this class cæsium and rubidium must be added.

#### 2nd Class.—*Metals decomposing water at* 100°.

Magnesium.
Cerium.
Lanthanum.
Didymium.
Glucinium.
Yttrium.
Erbium.
Terbium.
Zirconium.
Thorinum.
Aluminium.

These metals are generally known as metals of the earths.

3rd Class.—*Metals decomposing water at red heat, and disengaging hydrogen from cold water under the influence of dilute acids.*

Manganese.
Zinc.
Iron.
Nickel.
Cobalt.
Vanadium.
Cadmium.
Chromium.

4th Class.—*Metals decomposing water at red heat, and not disengaging hydrogen from cold water on contact with acids.*

Tin.
Antimony.
Uranium.
Titanium.
Molybdenum.
Tungsten.
Pelopium.
Niobium.
Tantalum.
Osmium.

5th Class.—*Metals which decompose water only at a white heat, and do not disengage hydrogen from cold water under the influence of acids.*

Copper.
Lead.
Bismuth.

### Second Section.

**Metals whose Oxides can be decomposed by heat alone.**

This section only contained one class in M. Thenard's original classification; M. Regnault divided it into two.

6th Class.—*Metals which do not decompose water at any temperature; which are capable of absorbing oxygen at a certain temperature, and whose oxides are reduced by a more intense heat.*

Mercury.
Rhodium.

7th Class.—*Metals which do not absorb oxygen at any temperature; which never decompose water, and whose oxides can be reduced by heat.*

Silver.
Gold.
Palladium.
Platinum.
Ruthenium.
Iridium.

This classification is no longer sufficient, for—

1st. In several classes many bodies appear which ought to be ranked among metalloids. The fourth class is almost entirely composed of such, we may perhaps say entirely, for it is very possible that pelopium ought to be placed by the side of tantalum, and that tungsten, molybdenum, and osmium may pass into the ranks of the metalloids.

2nd. Bodies which have manifest analogies in their properties are separated from each other in consequence of a difference observed in characteristics of secondary importance. It is thus that bodies like aluminium and iron are placed in different classes though presenting very great resemblances to each other.

3rd. Even from the arbitrary point of view taken by its author, this classification should be revised. Bodies such as aluminium and magnesium, which there appear as decomposing water at 100°, in reality only decompose it at red heat, as MM. Sainte-Claire Deville and Debray have demonstrated.

The rational classification would be one which would group metals according to their atomicity. Leaving to one side osmium and pelopium, which to all appearance are metalloids; indium and wasium, whose atomicity cannot be ascertained, and whose existence even is not certain, the following classification might be adopted:

### 1st Class. –*Monatomic metals.*

Silver.
Lithium.
Sodium.
Potassium.
Rubidium.
Cæsium.

### 2nd Class.—*Biatomic metals.*

Calcium.
Barium.
Strontium.
Magnesium.
Cerium.
Lanthanum.
Didymium.
Yttrium.
Erbium.
Terbium.
Thorinum.
Zinc.
Cadmium.
Copper.
Mercury.

### 3rd Class.—*Triatomic metals.*

Gold.
Thallium.
Vanadium.

### 4th Class.—*Tetratomic metals.*

Aluminium.
Glucinium.
Manganese.
Iron.
Chromium.
Cobalt.
Nickel.
Lead.
Platinum.
Palladium.

### 5th Class.—*Pentatomic metals.*

Up to the present time no metal belonging to this class has been discovered.

### 6TH CLASS.—*Hexatomic Metals.*

| | |
|---|---|
| Molybdenum. | Rhodium. |
| Tungsten. | Ruthenium. |
| Iridium. | |

In the first edition of this work we said:

"This classification is perhaps rather bold; several metals are here arranged as tetratomic whose compounds, corresponding to the formula $(MX^4)$, have never been obtained, only their compounds $(M^2X^6)$ being known. Several appear in this class without even their compounds of this latter character being known as yet. In the 6th class we have placed iridium and ruthenium, whose hexachlorides and bromides are not known.

"But if we admit, as I was the first to do, that the apparent atomicity of a body ought to be distinguished from its real atomicity, this being prevented from manifesting itself, in consequence of the weakness of its combining affinities; if, moreover, it be admitted, that when two bodies appear to have a different atomicity, they may nevertheless be considered as having an equal atomicity provided they present great analogies in their properties, we need not hesitate to accept the preceding classification.

"Nitrogen, on combining with hydrogen, chlorine, and other monatomic metalloids, only forms compounds corresponding to the formula $(NX^3)$, while phosphorus forms with chlorine the compound $(PCl^5)$.

"Let us suppose the acids which combine with ammonia and complete the group $(NX^5)$ to be unknown, nitrogen would be called triatomic, and phosphorus pentatomic.

"Starting from the known pentatomicity of phosphorus, nitrogen might be considered as pentatomic, and, in fact, this would be correct, because we know by the ammoniacal salts that such is the atomicity of this body.

"I suppose that, with regard to a great number of bodies, we are in the same position as we should be with nitrogen if these ammoniacal salts were unknown, and I establish the atomicity of these bodies by basing my arguments on the relations which they present to other bodies whose atomicity cannot be doubted.

"I also—basing my opinion on the fact that two atoms of any atomicity whatsoever, on combining with one another lose two units of their attractive power—affirm that a body which gives compounds of the order $(M^2X^6)$ is tetratomic. It is really necessary that M be tetratomic in order that the group $M^2$ may have an atomicity equal to 6.

"I know that my reasoning rests on hypothesis. But when is this not the case in science? Is the atomic theory itself anything but an hypothesis?

"My hypothesis takes into account all the facts, while it allows us to leave the old track, rejecting the old classification of metals, and adopting a new one. This alone entitles it to be taken into consideration."

Since the first edition was published, experience has justified our hypothesis. M. Niklès, having succeeded in giving stability to the less stable metallic chlorides by combining them with ethers, has demonstrated the existence of chloride of manganese ($MnCl^4$). The tetratomicity of manganese is therefore now certain, and analogy no longer allows us to doubt that metals of the same group are, like it, tetratomic.

## GENERAL PROPERTIES OF METALS.

Metals are all opaque; but, like all other properties, this one has its limits. When reduced to extreme tenuity they become translucent. Thus, gold leaf allows a green light to pass through it.

The colour of metals seen by transmitted light ought to be complementary to that seen when they are viewed by reflected light: this would cause us to expect gold to have a red colour when seen by reflected light, since red is complementary to green, which conclusion appears contrary to the fact. Nevertheless, if we cause a ray of light to be reflected eight or ten times from the surface of gold before receiving it into the eye, we perceive that the metal does acquire a red colour, which would not be observed after only a single reflection, but which, notwithstanding, is its true colour. The colour of a body seen by reflection arises in reality from the body absorbing rays the whole of which forms a shade complementary to that thus observed. If the absorption of these rays be easy, a single reflection is sufficient to give to the body the shade it ought to acquire, but if the absorption be difficult, the body only acquires its definite colour after the same ray has been reflected several times. This is the case with gold, and several other metals, such as copper, which is bright scarlet; silver, which is yellow: zinc, which is indigo blue; iron, which is violet, etc., in contradiction to what ordinary observation appears to demonstrate.

Almost all metals can crystallize, and they usually crystallize in the regular system, but all have not the same tendency to assume a crystalline structure. Generally this tendency diminishes with their tenacity. Some metals may be brought to the state of thin leaf by being passed between rollers, or by hammering; they are then called malleable. Others, on the contrary, always break when we try to flatten them; they are then called brittle. Only the first can be utilised in the uncombined state.

Malleable metals can not only be made into sheets, but they can also be drawn into wires. For this purpose a hard steel plate is used which is pierced with holes diminishing in size by regular gradation: this apparatus has been termed a draw-plate. After having roughly rounded the metal, it is made thinner at one end either by means of the hammer or by filing, and this end is placed in the largest hole in the draw-plate. It is seized by pincers on the other side and the metal drawn through. On repeating this operation through all the holes in the draw-plate, wires are obtained of great tenuity.

With certain metals we can go even beyond this. If a very fine platinum wire be placed inside a cylinder of silver, and the whole drawn through the draw-plate, a wire is obtained of a diameter equal to that of the original platinum wire; the outside of this wire is silver, but the centre is an axis of platinum: on boiling in nitric acid the silver is dissolved, and there remains a platinum wire of most extreme tenuity.

Metals must possess tenacity in order to be drawn into wire, or they cannot resist the traction without breaking, and the result is that all metals which can be made into thin leaves cannot be reduced to very fine wires. In order to distinguish these two properties, the first has retained the name of *malleability*, and the second is called *ductility.*

This difference is shown in the following table, where a certain number of bodies are successively disposed in the order of their greatest malleability and of their greatest ductility.

Order of greatest Malleability.

1. Gold.
2. Silver.
3. Copper.
4. Tin.
5. Platinum.
6. Lead.
7. Zinc.
8. Iron.
9. Nickel.

Order of greatest Ductility.

1. Gold.
2. Silver.
3. Platinum
4. Iron.
5. Nickel.
6. Copper.
7. Zinc.
8. Tin.
9. Lead.

Generally, when metals are reduced into leaves or wires, at a certain point they become brittle, and are then said to be hardened, and this hardening is always accompanied by disengagement of heat. On heating metals thus hardened, the caloric they had lost is restored, and with it their original flexibility. This operation is called tempering.

All metals are good conductors of heat and electricity, but there are also great differences between them in this respect.

On the temperature being raised sufficiently high all metals can be melted. Until late years, few of them could be reduced into vapour and distilled, but M. Henry Sainte-Claire Deville has volatilized nearly all by means of the oxyhydrogen blowpipe.

The density of metals is generally greater than that of water, but the alkaline metals are an exception.

**Alloys.**—When two metals are alloyed, the properties of the alloy are not intermediate between those of the two metals united; they are new and perfectly distinct properties. Thus the alloy may be harder than each of the metals which form it, and its density may be greater than the mean density of its elements, etc. These characteristics show that alloys are true definite combinations, though it is often difficult to separate such compounds in a pure state and to determine their formulas.

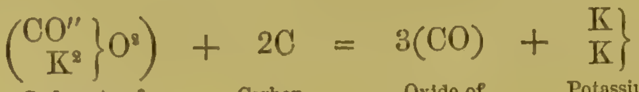
Most of the compounds actually employed in manufactures under the name of alloys containing tin, antimony, or bismuth, which are metalloids, ought to cease to bear the name. Nevertheless, as a name is of very little importance, and as, without endangering the theory, we can designate the compounds containing metalloids by the same appellation as if they only contained metals, we will continue to call these bodies alloys in order to conform to the nomenclature in use.

## FIRST CLASS (MONATOMIC METALS).

### POTASSIUM $\left.\begin{matrix}K\\K\end{matrix}\right\}$

Atomic weight = 39. Probable molecular weight = 78.

Davy first obtained potassium by decomposing a highly-concentrated solution of potash by means of a powerful galvanic battery, the negative pole of which was plunged into mercury placed at the bottom of that solution. The metal was resolved into an amalgam, and remained pure when this amalgam was submitted to the action of heat and the mercury driven off. Later, Gay-Lussac and Thenard obtained the metal by causing red-hot iron to act on melted potash. But now this body is prepared by strongly calcining in an iron bottle an intimate mixture of carbonate of potassium and charcoal (black flux), resulting from the calcination of cream of tartar. The potassium distils, and is received into an apparatus containing naphtha:



$$\left(\left.\begin{matrix}CO''\\K^2\end{matrix}\right\}O^2\right) + 2C = 3(CO) + \left.\begin{matrix}K\\K\end{matrix}\right\}$$

Carbonate of potassium. Carbon. Oxide of carbon. Potassium.

The potassium is melted under oil of naphtha to purify it; it is filtered through a cloth which is introduced into this oil, and finally it is again distilled.

Potassium is a white metal which soon tarnishes in the air; it is very soft, melts at 58°, and its density is 0·86. It is one of the bodies having the greatest affinity for oxygen of any with which we are acquainted, though cæsium and rubidium have still greater affinity for this metalloid. It absorbs dry oxygen at the ordinary temperature, and combines with it when hot still more easily.

It decomposes water at the ordinary temperature, and develops sufficient heat to produce the combustion of the hydrogen disengaged. The flame is coloured violet by a small quantity of vapour of potassium. When a globule of potassium is thrown on water, this phenomenon of combustion is at once observed, and the red-hot metal floats on the surface of the liquid. When the combustion ceases, a small globule of potash very hot, previously held up by the hydrogen gas, falls into the cold water and bursts, and its fragments are thrown in all directions by the vapour then produced. The great ease with which potassium oxidizes, obliges chemists to keep it beneath naphtha (carbide of hydrogen), which is a body entirely free from oxygen.

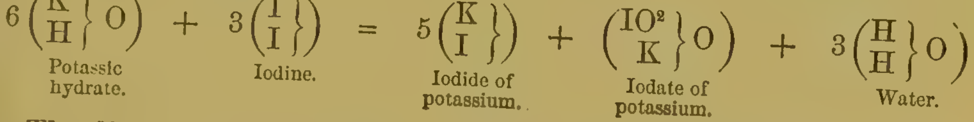
### Combinations of Potassium with Monatomic Metalloids.

Potassium on uniting with monatomic metalloids forms a single series of compounds answering to the formula (KR). We know the chloride of potassium (KCl), the bromide (KBr), the iodide (KI), and the fluoride (KFl).

**Chloride of Potassium** (KCl).—This is obtained as a refuse product in several manufactures, and a great quantity is extracted from the ashes of burnt seaweed, which yield as much as 30 per cent.

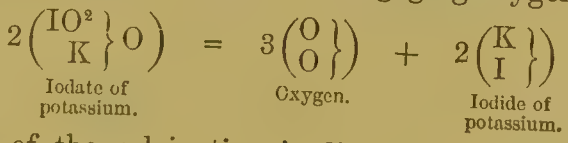
Chloride of potassium crystallizes in rectangular prisms; its density is 1·84. It is salt and bitter; 100 parts of water at 2° dissolve 29·2 parts, and 59·3 at the boiling temperature. Fifty grammes of this salt well-powdered, rapidly dissolves in 200$^{gr}$ of water contained in a vase weighing 185$^{gr}$, lowering the temperature to $-11{\cdot}4°$.

**Iodide of Potassium.**—This body may be obtained by several processes, the most simple of which consists in dissolving iodine in a concentrated solution of potash until the liquid is slightly coloured. Iodide of potassium is formed which remains dissolved, and potassic iodate which is precipitated. The reaction takes place according to the following equation:



$$\underset{\text{Potassic hydrate.}}{6\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} + \underset{\text{Iodine.}}{3\left(\left.\begin{matrix}I\\I\end{matrix}\right\}\right)} = \underset{\text{Iodide of potassium.}}{5\left(\left.\begin{matrix}K\\I\end{matrix}\right\}\right)} + \underset{\text{Iodate of potassium.}}{\left(\left.\begin{matrix}IO^2\\K\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

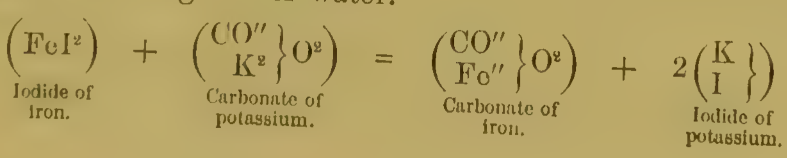
The liquor is evaporated to dryness without separating the precipitated iodate, and the residue is calcined at red heat: the iodate during the operation is changed into iodide, disengaging oxygen:



$$\underset{\text{Iodate of potassium.}}{2\left(\left.\begin{matrix}IO^2\\K\end{matrix}\right\}O\right)} = \underset{\text{Oxygen.}}{3\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\right)} + \underset{\text{Iodide of potassium.}}{2\left(\left.\begin{matrix}K\\I\end{matrix}\right\}\right)}$$

The residue of the calcination is dissolved in water and crystallized.

Iodide of potassium may also be prepared by precipitating, by potassic carbonate, the solution of iodide of iron obtained by pounding iodine and iron filings under water.



$$\underset{\text{Iodide of iron.}}{\left(FeI^2\right)} + \underset{\text{Carbonate of potassium.}}{\left(\left.\begin{matrix}CO''\\K^2\end{matrix}\right\}O^2\right)} = \underset{\text{Carbonate of iron.}}{\left(\left.\begin{matrix}CO''\\Fe''\end{matrix}\right\}O^2\right)} + \underset{\text{Iodide of potassium.}}{2\left(\left.\begin{matrix}K\\I\end{matrix}\right\}\right)}$$

Iodide of potassium crystallizes in colourless anhydrous cubes. It has a disagreeable bitter taste, and is fusible, deliquescent, soluble in alcohol, and very soluble in water, by dissolving in which it can cause a reduction of temperature to −24°.

Iodide of potassium is often adulterated with chloride of potassium or sodium. To detect this, a small quantity is dissolved in water, and nitrate of palladium is added to the solution till it no longer causes any precipitation. The solution is then filtered and treated with a solution of nitrate of silver. If this now causes a precipitate, it cannot arise from iodine, which has been wholly eliminated by the salt of palladium, and we may be certain that the salt examined contained a chloride.

Iodide of potassium is much used in medicine.

**Bromide of Potassium** ($KBr$).—Bromide of potassium is prepared like the iodide, with the single difference that bromine is substituted for iodine.

### COMPOUNDS OF POTASSIUM WITH POLYATOMIC METALLOIDS.

These metalloids combine with potassium in different proportions. Three oxides are known ($K^2O$), ($K^2O^2$), and ($K^2O^4$)*, and the sulphides ($K^2S$), ($K^2S^2$), ($K^2S^3$), ($K^2S^4$), and ($K^2S^5$).

Of the three oxides, the two last possess little stability, and on contact with water give potassic hydrate, at the same time disengaging oxygen.

$$\underset{\text{Tetr-oxide of potassium.}}{2(K^2O^4)} + \underset{\text{Water.}}{2(H^2O)} + \underset{\text{Potassic hydrate.}}{4\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} + \underset{\text{Oxygen.}}{3\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\right)}$$

**Protoxide of Potassium** ($K^2O$).—The best method of obtaining this body consists in heating very dry hydrate of potassium in a silver crucible with a quantity of potassium equal to that which the hydrate contains.

$$\underset{\text{Hydrate of potassium.}}{2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} + \underset{\text{Potassium.}}{\left.\begin{matrix}K\\K\end{matrix}\right\}} = \underset{\text{Protoxide of potassium.}}{2\left(\left.\begin{matrix}K\\K\end{matrix}\right\}O\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}}$$

Potassium may also be heated in oxygen, so as to obtain a tetr-oxide of this metal, and this tetr-oxide may afterwards be calcined in a silver crucible with a quantity of potassium equal to three times that which it contains.

$$\text{1st.}\quad \underset{\text{Potassium.}}{\left.\begin{matrix}K\\K\end{matrix}\right\}} + \underset{\text{Oxygen.}}{2\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\right)} = \underset{\text{Tetr-oxide of potassium.}}{\left.\begin{matrix}K\\K\end{matrix}\right\}O^4}$$

$$\text{2nd.}\quad \underset{\text{Tetr-oxide of potassium.}}{\left(\left.\begin{matrix}K\\K\end{matrix}\right\}O^4\right)} + \underset{\text{Potassium.}}{3\left(\left.\begin{matrix}K\\K\end{matrix}\right\}\right)} = \underset{\text{Protoxide of potassium.}}{4\left(\left.\begin{matrix}K\\K\end{matrix}\right\}O\right)}$$

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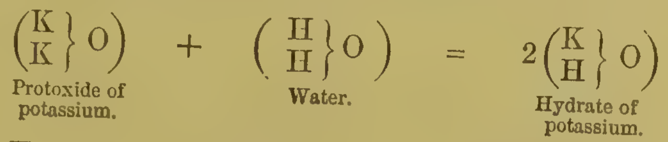
* H. Vernon Harcourt, *Quarterly Journal of the Chemical Society*, vol. xv., p. 276. October, 1861.

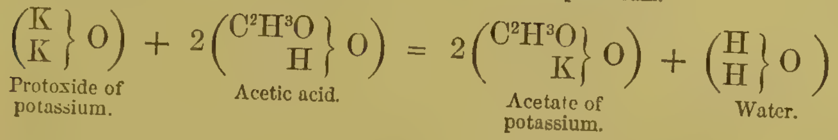
Protoxide of potassium is a powerful basic anhydride; it enters into double decomposition with water and with acids, giving a hydrate in the first case, and a potassic salt in the second.

1st.



$$\underset{\text{Protoxide of potassium.}}{\left(\left.\begin{matrix}K\\K\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = 2\underset{\text{Hydrate of potassium.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)}$$

2nd.



$$\underset{\text{Protoxide of potassium.}}{\left(\left.\begin{matrix}K\\K\end{matrix}\right\}O\right)} + 2\underset{\text{Acetic acid.}}{\left(\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O\right)} = 2\underset{\text{Acetate of potassium.}}{\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

The protoxide of potassium is not utilized, its only interest is as the anhydride of a powerful base.

**Hydrate of Potassium (Caustic Potash)** (KHO).—Hydrate of potassium, better known as caustic potash, is one of the most powerful bases known. It is a white substance, having a bright fracture and a burning acrid taste, a urinous smell, and is soapy to the touch.

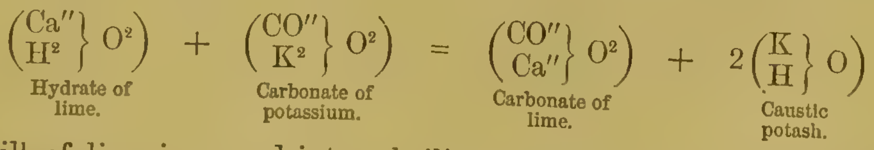
Potassic hydrate is only dehydrated when fused for a very long time and at a high temperature; and even then the greater part is volatilized without altering. The dehydrated part, which is protoxide of potassium, immediately absorbs oxygen from the air, and is transformed into the tetraoxide of the metal.

Hydrate of potassium is very soluble in water, and its solution is accompanied by a considerable disengagement of heat.

Hydrate of potassium is produced when water is decomposed by potassium:

$$\underset{\text{Potassium.}}{\left.\begin{matrix}K\\K\end{matrix}\right\}} + 2\underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = 2\underset{\text{Potassic hydrate.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}}$$

But this method of preparation would be very expensive. Caustic potash is obtained in manufactures by decomposing carbonate of potash by hydrate of lime.



$$\underset{\text{Hydrate of lime.}}{\left(\left.\begin{matrix}Ca''\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Carbonate of potassium.}}{\left(\left.\begin{matrix}CO''\\K^2\end{matrix}\right\}O^2\right)} = \underset{\text{Carbonate of lime.}}{\left(\left.\begin{matrix}CO''\\Ca''\end{matrix}\right\}O^2\right)} + 2\underset{\text{Caustic potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)}$$

Milk of lime is poured into a boiling dilute solution of carbonate of potassium. When the quantity of lime added is sufficient for the double decomposition to be complete (which is known when a small quantity of the filtered liquor no longer effervesces with acids), it is left to settle: the carbonate of lime is deposited, and the solution of potash has then only to be decanted and evaporated. The evaporation should be effected in a silver pan. When all the water is evaporated the solid mass is melted, and poured into moulds.

As neither the carbonate of potassium nor the lime used is pure, the potash contains numerous impurities; in order to purify it, the potash of commerce is dissolved in alcohol and the solution evaporated. The impurities remain dissolved in the water which the alcohol contained, and form a layer, which cannot mix with the alcohol saturated with potash, and which therefore can be easily separated from it.

By means of hydrate of potash a great number of oxygenized salts can be formed: those we will mention are the carbonates, the nitrate, chlorate, hypochlorite, and sulphates of potassium.

**Neutral Carbonate of Potassium** $\left(\begin{matrix}CO''\\K^2\end{matrix}\right\} O^2\Big)$.—This salt is extracted by lixiviating the ashes of vegetables. It may be prepared artificially from the sulphate of potassium contained in sea water, by the same process as that used to prepare carbonate of sodium; but up to the present time, in spite of the advantages of such a proceeding, sulphate of potassium has not been extracted from sea water.

For laboratory purposes, in order to obtain pure carbonate of potassium, the bitartrate (which is easily obtained pure by crystallization) is calcined. This salt, which is of an organic nature, decomposes and leaves a residue of carbonate of potassium and carbon (black flux), the same as is used in the preparation of potassium. The black flux is treated by water, the potassic carbonate it contains is dissolved, the solution is filtered to separate the carbon, and evaporated to dryness. Instead of the bitartrate, the binoxalate of potassium may be used; the residue is then pure carbonate of potassium, with no traces of charcoal.

Carbonate of potassium is a white salt, very soluble in water, and deliquescent. Its reaction on test paper is alkaline. All acids decompose it with effervescence; carbonic anhydride is disengaged, and a new salt of potassium is formed.

$$\begin{array}{ccccccccc}(CK^2O^3) & + & (SH^2O^4) & = & (SK^2O^4) & + & (H^2O) & + & (CO^2)\\ \text{Carbonate of potassium.} & & \text{Sulphuric acid.} & & \text{Sulphate of potassium.} & & \text{Water.} & & \text{Carbonic anhydride.}\end{array}$$

We have seen that when a dilute solution of this salt is boiled with hydrate of calcium, double decomposition takes place, and carbonate of lime and caustic potash are formed. If the solution were concentrated, this reaction would not be produced. In this case, in fact, an inverse reaction takes place. Carbonate of calcium boiled with a highly-concentrated solution of caustic potash gives hydrate of lime and carbonate of potassium.

$$\begin{array}{ccccccc}\left(\begin{matrix}CO''\\Ca''\end{matrix}\right\} O^2\Big) & + & 2\left(\begin{matrix}K\\H\end{matrix}\right\} O\Big) & = & \left(\begin{matrix}Ca''\\H^2\end{matrix}\right\} O^2\Big) & + & \left(\begin{matrix}CO''\\K^2\end{matrix}\right\} O^2\Big)\\ \text{Carbonate of lime.} & & \text{Hydrate of potassium.} & & \text{Hydrate of lime.} & & \text{Carbonate of potassium.}\end{array}$$

Vapour of water at a high temperature partially transforms the carbonate into hydrate of potassium.

$$\underset{\text{Carbonate of potassium.}}{\left(\left.\begin{matrix}\mathrm{CO}''\\ \mathrm{K}^2\end{matrix}\right.\mathrm{O}^2\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} = 2\underset{\text{Caustic potash.}}{\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Carbonic anhydride.}}{\left(\mathrm{CO}^2\right)}$$

**Bicarbonate of Potassium** $\left(\left.\begin{matrix}\mathrm{CO}''\\ \mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}^2\right)$.—This salt is deposited in crystals when a current of carbonic anhydride is transmitted through a concentrated solution of neutral carbonate:

$$\underset{\text{Carbonate of potassium.}}{\left(\left.\begin{matrix}\mathrm{CO}''\\ \mathrm{K}^2\end{matrix}\right\}\mathrm{O}^2\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Carbonic anhydride.}}{\left(\mathrm{CO}^2\right)} = 2\underset{\text{Bicarbonate of potassium.}}{\left(\left.\begin{matrix}\mathrm{CO}''\\ \mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}^2\right)}$$

Bicarbonate of potassium crystallizes in right rhombic prisms: 100 parts of water dissolve 23·23 parts of it at 10°, and 26·91 at 20°. When boiled it loses water and carbonic anhydride, and is converted into neutral carbonate:

$$2\underset{\text{Bicarbonate of potassium.}}{\left(\left.\begin{matrix}\mathrm{CO}''\\ \mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}^2\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Carbonic anhydride.}}{\left(\mathrm{CO}^2\right)} + \underset{\text{Neutral carbonate of potassium.}}{\left(\left.\begin{matrix}\mathrm{CO}''\\ \mathrm{K}^2\end{matrix}\right\}\mathrm{O}^2\right)}$$

When pure it does not precipitate magnesium salts. It is much used in medicine.

**Nitrate of Potassium** $\left(\left.\begin{matrix}\mathrm{NO}^2\\ \mathrm{K}\end{matrix}\right\}\mathrm{O}\right)$.—This is a substance of very great importance. It is used in the preparation of gunpowder, and, besides, is much employed in medicine, and in numerous chemical processes.

This salt is found on the surface of the soil: in Peru there is a natural mixture of nitrate of potassium and sand, from which the nitrate is procured by simple lixiviation. In temperate climates nature produces less, but the soil contains nitrates of lime and magnesia. By lixiviating the materials which contain these nitrates, and precipitating the product by carbonate of potassium, potassic nitrate is obtained, which crystallizes on evaporating the liquor.

$$\underset{\text{Nitrate of lime.}}{\left(\mathrm{Ca}''\left\{\begin{matrix}\mathrm{ONO}^2\\ \mathrm{ONO}^2\end{matrix}\right.\right)} + \underset{\text{Carbonate of potassium.}}{\left(\left.\begin{matrix}\mathrm{CO}''\\ \mathrm{K}^2\end{matrix}\right\}\mathrm{O}^2\right)} = \underset{\text{Carbonate of lime.}}{\left(\left.\begin{matrix}\mathrm{CO}''\\ \mathrm{Ca}''\end{matrix}\right\}\mathrm{O}^2\right)} + 2\underset{\text{Nitrate of potassium.}}{\left(\mathrm{KONO}^2\right)}$$

It is, however, preferable to prepare the nitrate of potassium by decomposing the natural nitrate of sodium procured from Peru, by chloride of potassium. For this purpose, equivalent weights of these two salts are heated together in a large cauldron containing water; during the boiling, double decomposition takes place, and chloride of sodium and nitrate of potassium are formed.

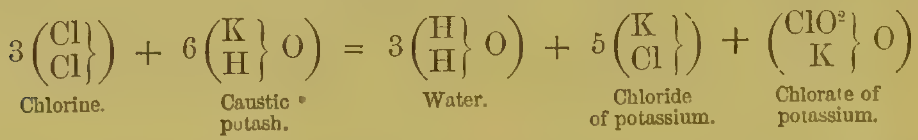
Chloride of sodium, being scarcely more soluble in hot than in cold water, the greatest part of this salt is deposited during the boiling, and removed; the nitrate of potassium, on the contrary, which is much more soluble in hot than in cold water, remains dissolved. The liquor is left to cool, when it ceases to deposit chloride of sodium, and the nitrate of potassium crystallizes. As this salt still contains some chloride of sodium, it is washed with a saturated solution of nitrate of potassium, which cannot dissolve any more of this latter body, but which takes up the chloride of sodium. In order to obtain perfectly pure nitrate of potassium, it must be crystallized several times by dissolving it in boiling water, and then allowing the liquor to cool.

Nitrate of potassium crystallizes in long six-sided prisms, terminated by hexahedral pyramids, which are always anhydrous: it melts at 350°, and does not again crystallize on regaining the solid state; its taste is first fresh and cooling, and then bitter and salt. It is an unstable body, easily yields its oxygen to combustible substances, and deflagrates when thrown on burning coals: on mixing it with powdered charcoal and sulphur, very combustible compounds are produced; and, as the products of the combustion of sulphur and carbon are gaseous, these mixtures, when ignited in a limited space, give, by the sudden expansion, great power of projection. Such mixtures form gunpowder. The combustible property of nitrate of potassium is often utilized in the laboratory. Nitrate of potassium is insoluble in alcohol; 100 parts of water at 0 dissolve 1·25 parts of the salt; at 18° they dissolve 29 parts, and at 100°, 250 parts. The saturated solution contains 315 of the salt to 100 of water, and boils at 116°.

Nitrate of potassium is a very powerful diuretic.

In commerce this salt is known as saltpetre, nitre, and nitrate of potash.

**Chlorate of Potassium** $\left(\left.\begin{matrix}ClO^2\\K\end{matrix}\right\}O\right)$.—This salt may be obtained by transmitting a current of chlorine through a concentrated solution of caustic potash; three molecules of chlorine and six molecules of potash enter into reaction; and there are formed three molecules of water, five molecules of chloride of potassium, and one molecule of chlorate.



$$\underset{\text{Chlorine.}}{3\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}\right)} + \underset{\text{Caustic potash.}}{6\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Water.}}{3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Chloride of potassium.}}{5\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)} + \underset{\text{Chlorate of potassium.}}{\left(\left.\begin{matrix}ClO^2\\K\end{matrix}\right\}O\right)}$$

Potassic chlorate being much less soluble in water than the chloride, crystallizes first, and it is perfectly purified by successive crystallizations.

It may also be prepared by transmitting chlorine into milk of lime, adding chloride of potassium to the liquor, boiling for some time, and then allowing it to cool. The chlorate of potassium is deposited in crystals.

In this reaction, the chlorine acting on the lime, first gives chloride of lime ($\text{CaOCl}^2$); this body on boiling gives chlorate of calcium, which enters into double decomposition with the potassic chloride.

1st.
$$6\underset{\text{Chloride of lime.}}{\left(\text{Ca}''\left\{\begin{matrix}\text{OCl}\\ \text{Cl}\end{matrix}\right.\right)} = 5\underset{\text{Chloride of calcium.}}{\left(\text{Ca}''\left\{\begin{matrix}\text{Cl}\\ \text{Cl}\end{matrix}\right.\right)} + \underset{\text{Chlorate of calcium.}}{\left(\text{Ca}''\left\{\begin{matrix}\text{O,ClO}^2\\ \text{O,ClO}^2\end{matrix}\right.\right)}$$

2nd.
$$\underset{\text{Chlorate of calcium.}}{\left(\text{Ca}''\left\{\begin{matrix}\text{O,ClO}^2\\ \text{O,ClO}^2\end{matrix}\right.\right)} + 2\underset{\text{Chloride of potassium.}}{\left(\left.\begin{matrix}\text{K}\\ \text{Cl}\end{matrix}\right\}\right)} = \underset{\text{Chloride of calcium.}}{\left(\text{Ca}''\left\{\begin{matrix}\text{Cl}\\ \text{Cl}\end{matrix}\right.\right)} + 2\underset{\text{Chlorate of potassium.}}{\left(\left.\begin{matrix}\text{ClO}^2\\ \text{K}\end{matrix}\right\}\text{O}\right)}$$

The chlorate of potassium formed is deposited from the solution on cooling.

Chlorate of potassium crystallizes in transparent anhydrous hexagonal laminæ; it is insoluble in alcohol; 100 parts of water dissolve 6·03 at 15°, and 60·24 at the boiling temperature. It melts at 400°. At a still higher temperature it disengages oxygen, and perchlorate and chloride of potassium are formed.

$$2\underset{\text{Chlorate of potassium.}}{\left(\left.\begin{matrix}\text{ClO}^2\\ \text{K}\end{matrix}\right\}\text{O}\right)} = \underset{\text{Perchlorate of potassium.}}{\left(\left.\begin{matrix}\text{ClO}^3\\ \text{K}\end{matrix}\right\}\text{O}\right)} + \underset{\text{Chloride of potassium.}}{\left(\begin{matrix}\text{K}\\ \text{Cl}\end{matrix}\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}\text{O}\\ \text{O}\end{matrix}\right\}}$$

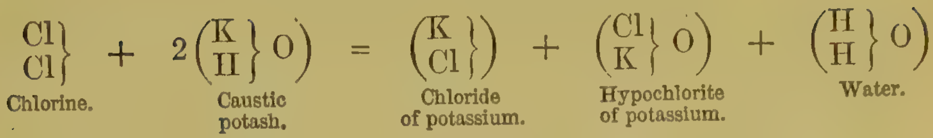
If still greater heat be applied, the perchlorate of potassium decomposes in its turn; all the oxygen is disengaged, and there remains only chloride of potassium.

$$\underset{\text{Perchlorate of potassium.}}{\left(\left.\begin{matrix}\text{ClO}^3\\ \text{K}\end{matrix}\right\}\text{O}\right)} = \underset{\text{Chloride of potassium.}}{\left(\left.\begin{matrix}\text{K}\\ \text{Cl}\end{matrix}\right\}\right)} + 2\underset{\text{Oxygen.}}{\left(\left.\begin{matrix}\text{O}\\ \text{O}\end{matrix}\right\}\right)}$$

The ease with which the potassic chlorate parts with its oxygen makes it very combustible; it fuses on glowing charcoal, and forms with combustible substances detonating mixtures. On mixing sulphur and chlorate of potassium, pounded separately, a powder is obtained, which detonates when struck with a hammer.

A mixture of chlorate of potassium, sulphur, and lycopodium (very inflammable pulverulent organic matter), takes fire when a drop of sulphuric acid is added.

**Hypochlorite of Potassium** (ClKO).—When, instead of directing a current of chlorine through a concentrated solution of hydrate of potassium, it is directed through a dilute solution of the same body, the reaction no longer takes place between three molecules of chlorine, and six of hydrate of potassium, but between one molecule of chlorine and two of potash; thus a mixture of potassic chloride and hypochlorite is formed.

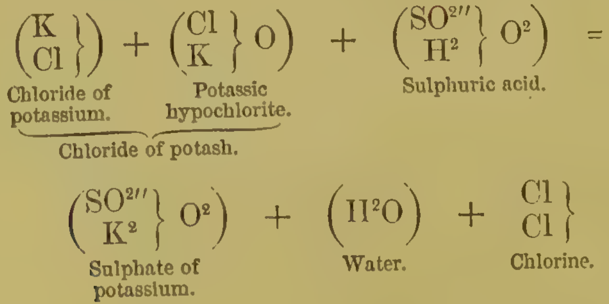


$$\underset{\text{Chlorine.}}{\left.\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right\}} + \underset{\text{Caustic potash.}}{2\left(\left.\begin{matrix}\mathrm{K}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\text{Chloride of potassium.}}{\left(\left.\begin{matrix}\mathrm{K}\\\mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\text{Hypochlorite of potassium.}}{\left(\left.\begin{matrix}\mathrm{Cl}\\\mathrm{K}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}$$

These two salts cannot be separated from each other.

The liquor which holds in solution this mixture of hypochlorite and chloride of potassium is known in the arts as Javelle water, or solution of chloride of potassium.

Under the influence of the weakest acids, even of carbonic anhydride, it parts with the whole of its chlorine; and is, therefore, employed as a disinfectant and for bleaching.

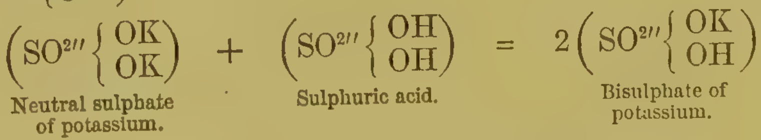


$$\underbrace{\underset{\text{Chloride of potassium.}}{\left(\left.\begin{matrix}\mathrm{K}\\\mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\text{Potassic hypochlorite.}}{\left(\left.\begin{matrix}\mathrm{Cl}\\\mathrm{K}\end{matrix}\right\}\mathrm{O}\right)}}_{\text{Chloride of potash.}} + \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}\mathrm{SO^{2\prime\prime}}\\\mathrm{H^2}\end{matrix}\right\}\mathrm{O^2}\right)} =$$

$$\underset{\text{Sulphate of potassium.}}{\left(\left.\begin{matrix}\mathrm{SO^{2\prime\prime}}\\\mathrm{K^2}\end{matrix}\right\}\mathrm{O^2}\right)} + \underset{\text{Water.}}{\left(\mathrm{H^2O}\right)} + \underset{\text{Chlorine.}}{\left.\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right\}}$$

**Neutral Sulphate of Potassium** $\left(\left.\begin{matrix}\mathrm{SO^{2\prime\prime}}\\\mathrm{K^2}\end{matrix}\right\}\mathrm{O^2}\right)$.—This salt may be extracted from sea-water, but this method is not generally used; it is prepared artificially by treating carbonate of potassium with sulphuric acid: the sulphate of potassium crystallizes in anhydrous six-sided prisms terminating in hexahedral pyramids; at a high temperature it melts without decomposing; 100 parts of water dissolve 10·5 at 12°, 7 at 26°, and 3 at 100°; it is quite insoluble in alcohol.

**Bisulphate of Potassium** $\left(\mathrm{SO^{2\prime\prime}}\left\{\begin{matrix}\mathrm{OK}\\\mathrm{OH}\end{matrix}\right.\right)$.—This salt may be prepared by heating the neutral sulphate with half its weight of normal sulphuric acid; as soon as the fumes of the sulphuric acid cease, it is allowed to cool, and the residue is dissolved in water. When this liquid is evaporated, colourless prismatic crystals of the bisulphate of potassium $\left(\mathrm{SO^{2\prime\prime}}\left\{\begin{matrix}\mathrm{OK}\\\mathrm{OH}\end{matrix}\right.\right)$ form.



$$\underset{\text{Neutral sulphate of potassium.}}{\left(\mathrm{SO^{2\prime\prime}}\left\{\begin{matrix}\mathrm{OK}\\\mathrm{OK}\end{matrix}\right.\right)} + \underset{\text{Sulphuric acid.}}{\left(\mathrm{SO^{2\prime\prime}}\left\{\begin{matrix}\mathrm{OH}\\\mathrm{OH}\end{matrix}\right.\right)} = \underset{\text{Bisulphate of potassium.}}{2\left(\mathrm{SO^{2\prime\prime}}\left\{\begin{matrix}\mathrm{OK}\\\mathrm{OH}\end{matrix}\right.\right)}$$

As the bisulphate of potassium only decomposes at 600°, it is used in analyses for the purpose of acting on certain minerals which escape the action of sulphuric acid, on account of its boiling point being much lower (325°).

Bisulphate of potassium loses water by heat, and is transformed into disulphate, which, heated still more, leaves sulphuric anhydride, and returns to the state of neutral sulphate.

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$$\text{1st.}\quad \underset{\text{Bisulphate of potassium.}}{2\left(SO^{2''}\left\{\begin{matrix}OK\\OH\end{matrix}\right.\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Disulphate of potassium.}}{\left(\begin{matrix}SO^{2''}\\SO^{2''}\end{matrix}\left\{\begin{matrix}OK\\O\\OK\end{matrix}\right\}\right)}$$

$$\text{2nd.}\quad \underset{\text{Potassic disulphate.}}{\left(\begin{matrix}SO^{2''}\\SO^{2''}\end{matrix}\left\{\begin{matrix}OK\\O\\OK\end{matrix}\right\}\right)} = \underset{\text{Neutral sulphate of potassium.}}{\left(SO^{2''}\left\{\begin{matrix}OK\\OK\end{matrix}\right.\right)} + \underset{\text{Sulphuric anhydride.}}{\left(SO^{2''},O\right)}$$

**Monosulphide of Potassium** ($K^2S$).—The monosulphide of potassium is obtained by dividing a solution of hydrate of potassium into two equal parts, supersaturating one part by hydrosulphuric acid, and then adding the other portion of the solution; hydrosulphide of potassium is produced, which on contact with the hydrate of the same metal, gives water and monosulphide.

$$\text{1st.}\quad \underset{\text{Hydrate of potassium.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} + \underset{\text{Hydrosulphuric acid.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}S\right)} = \underset{\text{Hydrosulphate of potassium.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}S\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

$$\text{2nd.}\quad \underset{\text{Hydrate of potassium.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} + \underset{\text{Hydrosulphate of potassium.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}S\right)} = \underset{\text{Sulphide of potassium.}}{\left(\left.\begin{matrix}K\\K\end{matrix}\right\}S\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

The monosulphide of potassium is to the corresponding hydrosulphide, what the oxide of potassium is to caustic potash.

| | |
|---|---|
| ($K^2O$)<br>Oxide of potassium. | ($KHO$)<br>Hydrate of potassium. |
| ($K^2S$)<br>Sulphide of potassium. | ($KHS$)<br>Hydrosulphide of potassium. |

The hydrosulphide of potassium being a powerful sulpho-base, the nonosulphide of this metal is a basic anhydrosulphide.

**Characteristics of Potassic Salts.**—These salts are recognized by he following characters.

1st. Alkaline carbonates do not precipitate them.

2nd. In presence of tartaric acid, their solutions give a bitartrate vhich is slightly soluble in cold water, and which precipitates when he liquid is shaken.

3rd. Hydrofluosilicic and perchloric acids precipitate them; the preci- itate formed by the former is gelatinous and assumes a beautiful white olour when dried in free air.

4th. The bichloride of platinum causes the formation of a yellow recipitate of double chloride of platinum and potassium. If the lution be greatly diluted, a little alcohol must be added for the pre- pitate to form. This double chloride decomposes when heated into loride of potassium and spongy metallic platinum.

5th. Sulphate of potassium is anhydrous, and remains unchanged the air, and the carbonate is deliquescent.

## SODIUM $\left.\begin{matrix}Na\\Na\end{matrix}\right\}$

Atomic weight = 23. Probable molecular weight = 46.

Sodium so much resembles potassium that to give the history of one is almost to give that of the other. The affinities are of the same nature, except that those of sodium are a little weaker. Like potassium, it decomposes water at the ordinary temperature; but the elevation of temperature produced being less, the hydrogen does not ignite unless the water have gum added to it, so that the metal, being no longer able to move on its surface, does not lose its heat so quickly.

In physical properties also they much resemble each other. Sodium melts at 90°, has a density equal to 0·972, and is soft at the ordinary temperature.

The preparation is the same, with the slight difference that the mixture of carbonate of sodium and carbon need not be so intimate as that of the carbonate of potassium and carbon. It may be prepared directly by mixing the two bodies after they have been pulverized.

Sodium also combines with biatomic metalloids: with sulphur it gives the same compounds as potassium; with oxygen, like this latter metal, it gives a protoxide ($Na^2O$) and a binoxide ($Na^2O^2$); the tetroxide ($Na^2O^4$) which would correspond to the tetroxide of potassium has not yet been obtained.

A basic hydrate and numerous salts correspond to the protoxide of sodium as in the case of potassium.

Of all the sodic compounds, the only ones which require our attention are: the chloride, hydrate, neutral sulphate and acid sulphate, neutral carbonate, bicarbonate and sesquicarbonate, the nitrate, borate, and hypochlorite.

**Chloride of Sodium** (Common Salt) ($NaCl$).—This body can be prepared artificially by saturating the hydrate or carbonate of sodium by hydrochloric acid, or by submitting sodium to the action of hydrochloric acid or chlorine. But this is unnecessary; the chloride of sodium exists in nature in such very great abundance that, so far from its being produced artificially, it is the primitive substance from which all the compounds of sodium are obtained.

Chloride of sodium crystallizes in cubes which are grouped in small pyramids hollow in the interior. Its crystals do not contain any water of crystallization; when exposed to heat they decrepitate and then melt, and are reduced to vapour if the temperature be sufficiently elevated.

The density of chloride of sodium is 2·13. One part of this body requires 2·79 of water at 13° to dissolve it, and 2·45 at the boiling temperature. Its solubility is therefore hardly greater in hot than in cold water. At $-12°$ a concentrated solution deposits prismatic crystals containing two molecules of water whose formula is ($NaCl + 2$ aq.).

Pure chloride of sodium is not deliquescent unless the hygrometer marks more than 86°, but the presence of chloride of magnesium gives it the property of attracting the moisture of the air much below this hygrometric degree. It is used for food under the name of sea or kitchen salt.

EXTRACTION OF CHLORIDE OF SODIUM.—Chloride of sodium exists in salt water and in some salt springs, and besides there are considerable deposits in the earth known as rock salt mines. The best known are those of Wielitzka in Poland and Cardona in Spain, but there are other important beds in Sicily and in the republic of New Granada. When rock salt is pure, it is extracted by shafts and galleries like other minerals, and it is then pulverized and made fit for sale. When it is impure, it is dissolved in the mine by means of fresh water, and then purified by crystallization. Whatever may be the processes used to bring the fresh water into the mine, and to remove the salt water, this latter must be concentrated for the salt to crystallize; this concentration takes place in pans disposed so that they lose as little heat as possible. During the concentration, the salt is deposited in small crystals; in order to obtain it still purer, the crystallization is disturbed by stirring the liquid with a small rod, which at the same time serves to extract the salt already deposited. After some time, the pans become covered with a layer of double sulphate of potassium and lime, which compels the work to be stopped for its removal, because as soon as a rather thick layer is formed it prevents the transmission of heat. Sea water from which the salt is deposited contains the chlorides of calcium and magnesium.

When the salt is extracted from salt springs, the water must first be concentrated; it would be too poor, and require too much fuel for its concentration by heat to be profitable. This concentration is effected by means of what are called graduation buildings.

These buildings (fig. 33, p. 214) are only a kind of wall formed of bundles of faggots held together by wooden frames. The whole is covered with a shed. They are placed on clayed soil surrounded by stones, forming a large basin. Their direction is such that they are exposed at right angles to the wind ordinarily prevailing in the country.

A trench which surrounds the top of each wall allows the water pumped up to flow by side openings on to the bundles of faggots. This water descends into the lower basin, and in passing through these bundles presents a large surface for evaporation. After having being transmitted thus through five or six successive buildings, the water is generally rich enough to be concentrated in the pans.

This concentration is made in the manner described when speaking of rock salt. Nevertheless, as here the waters are less pure, the work is divided into two operations.

In the first (schlotage) the liquid is boiled briskly, which produces the separation of a double sulphate of sodium and calcium (schlot), which is taken away as it forms. When the chloride of sodium commences to deposit, the temperature is lowered to prevent the sulphate of magnesia crystallizing at the same time. As the concentration proceeds, the mother liquors become charged with different salts, till at last the salt which deposits is impure, when the mother liquor is thrown away and the operation is recommenced.

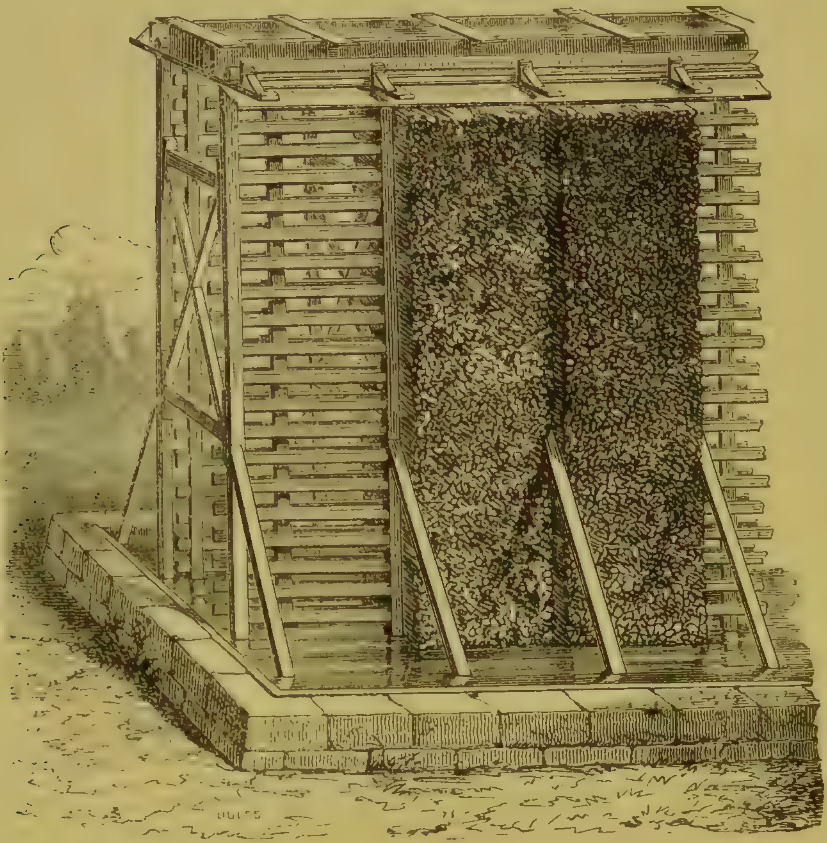


Fig. 33.

This process may be improved by adding a certain quantity of lime, at the commencement, to the liquors. Calcium takes the place of magnesium, which abounds in these waters in the state of chloride and sulphate, and magnesic hydrate precipitates. The calcium passes to the state of chloride and sulphate; sulphate of sodium is also present, with which the chloride of calcium enters into double decomposition, the products being chloride of sodium and sulphate of lime.

A double sulphate of sodium and lime (schlot) is deposited during the schlotage, and when the formation of salt is commenced, the liquors are freed from the salts of magnesia, which would interfere with the operation.

The chloride of sodium may also be extracted from sea water.

At high tide the water is brought into a large basin of 800 to 1000 square metres of surface, and of 60 centimetres to 2 metres in depth. It is allowed to remain in the basin until it gets heated and deposits the impurities held in suspension.

The water is then brought by a subterranean canal into a series of basins whose depth is from 25 to 45 centimetres, and the superficial area about 400 square metres. These basins communicate with each other by small openings, and as the inclination is very slight, the water only runs through them extremely slowly.

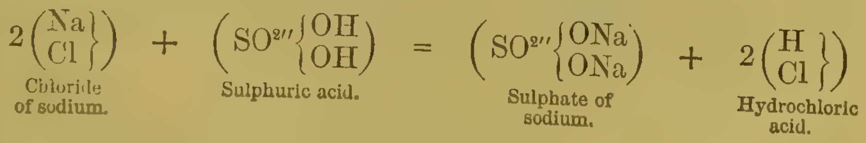
After leaving this first series of basins, the water passes by a trench into a second series of only eight basins, the surface of which is less extended than that of the preceding series.

After passing this second series, the water goes into a third formed of four basins, the surface of which is as extended as that of the preceding eight. Here the water is sufficiently concentrated; small trenches at the sides allow it to pass into spaces placed to the right and left where the salt is deposited.

This salt is placed in a heap formed like a truncated cone, surmounted by a spherical top. This heap is covered with clay to preserve it from the rain, while the mass is maintained in a sufficient state of humidity to cause the deliquescent salts, as chloride of magnesium, to liquefy and run into the trenches situated at the lower part of the heap. The chloride of sodium thus obtained is in small greyish crystals. In order to purify it and render it white, it must be washed with water saturated with sea salt, which dissolves its impurities only.

The mother liquors from which sea salt is extracted also contain other salts. M. Balard has shown that sulphate of potassium may also be extracted, but the limits of this work do not permit us to describe his process. The extraction of sulphate of potassium from the mother liquors of saline springs is extensively carried on in France.

**Neutral Sulphate of Sodium (Glauber's Salts)** $\left(SO^{2''}\left\{\begin{matrix}ONa\\ONa\end{matrix}\right.\right)$.—This salt is prepared by heating chloride of sodium with sulphuric acid; hydrochloric acid is also produced in this reaction.



$$\underset{\text{Chloride of sodium.}}{2\left(\begin{matrix}Na\\Cl\end{matrix}\right\}\right)} + \underset{\text{Sulphuric acid.}}{\left(SO^{2''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)} = \underset{\text{Sulphate of sodium.}}{\left(SO^{2''}\left\{\begin{matrix}ONa\\ONa\end{matrix}\right.\right)} + \underset{\text{Hydrochloric acid.}}{2\left(\begin{matrix}H\\Cl\end{matrix}\right\}\right)}$$

Sulphate of sodium is insoluble in alcohol; 100 parts of water dissolve 50·65 at 32°, and do not dissolve more than 42·65 at 103°. Its solubility increases from 0° to 33°, and decreases from 33° as the temperature rises; we have already seen (*see* Solubility) how this curious fact may be explained.

We can very easily obtain a highly-supersaturated solution of this salt.

Sulphate of sodium is deposited from its aqueous solution in large four-sided prisms, terminated by dihedral summits. These crystals contain ten molecules of water of crystallization, their formula is

$$\left(SO^{2''}\left\{\begin{matrix}ONa\\ONa\end{matrix}\right. + 10\text{ aq.}\right)$$

It may also be obtained crystallized with different quantities of water, by varying the temperature at which it is deposited from its solution.

Sulphate of sodium effloresces in the air, giving off water: when heated it undergoes, first, aqueous fusion; then its water of crystallization evaporating, the salt again becomes solid. At a much higher temperature it undergoes igneous fusion.

Sulphate of sodium is employed in medicine as a purgative; in manufactures it is used for the preparation of carbonate of sodium.

**Bisulphate of Sodium** $\left(SO^{2''}\left\{\begin{matrix}ONa\\OH\end{matrix}\right. + 2\text{ aq.}\right)$.—This salt is prepared by means of neutral sulphate of sodium, like the bisulphate of potassium, from the neutral sulphate of that metal. Its properties are the same as those of bisulphate of potassium.

**Neutral Carbonate of Sodium** $\left(CO''\left\{\begin{matrix}ONa\\ONa\end{matrix}\right.\right)$.—Carbonate of sodium, which is the foundation of a great number of sodic compounds, was formerly extracted from the ashes of vegetables that grow on the sea-coast. At the present time it is prepared by means of the sulphate which is obtained, as we have just seen, by means of the chloride of sodium. In order to transform the sulphate into carbonate of sodium, the first of these salts is heated in oval furnaces, after having been intimately mixed with carbonate of lime and coal. Sulphide of sodium is formed by the reaction of the carbon of the coal on the sulphate of sodium.

$$\underset{\text{Sulphate of sodium.}}{\left(SO^{2''}\left\{\begin{matrix}ONa\\ONa\end{matrix}\right.\right)} + \underset{\text{Carbon.}}{2C} = \underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{2\left(CO^2\right)} + \underset{\substack{\text{Sulphide of}\\\text{sodium.}}}{\left(\left.\begin{matrix}Na\\Na\end{matrix}\right\}S\right)}$$

The sulphide of sodium then reacts on the carbonate of lime, and gives a mixture of carbonate of sodium and sulphide of calcium, the latter of which is very slightly soluble in water.

$$\underset{\substack{\text{Sulphide of}\\\text{sodium.}}}{\left(\left.\begin{matrix}Na\\Na\end{matrix}\right\}S\right)} + \underset{\substack{\text{Carbonate of}\\\text{lime.}}}{\left(\left.\begin{matrix}CO''\\Ca''\end{matrix}\right\}O^2\right)} = \underset{\substack{\text{Carbonate of}\\\text{sodium.}}}{\left(\left.\begin{matrix}CO''\\Na^2\end{matrix}\right\}O^2\right)} + \underset{\substack{\text{Sulphide}\\\text{of calcium.}}}{\left(Ca''S\right)}$$

Water is used to dissolve the carbonate of sodium, and separate it from the sulphide of calcium; the water is evaporated, and the alkaline salt is crystallized. According to M. Scheurer-Kestner, who has recently studied this question, the definite equation of the formation of carbonate of sodium would be the following:—

LEEDS SCHOOL OF MEDICINE

1st. $$\underset{\text{Sulphate of sodium.}}{5(Na^2SO^4)} + \underset{\text{Carbon.}}{10C} = \underset{\text{Sulphide of sodium.}}{5(Na^2S)} + \underset{\text{Carbonic anhydride.}}{10(CO^2)}$$

2nd. $$\underset{\text{Sulphide of sodium.}}{5(Na^2S)} + \underset{\text{Carbonate of calcium.}}{7(CaCO^3)} = \underset{\text{Carbonate of sodium.}}{5(Na^2CO^3)} + \underset{\text{Sulphide of calcium.}}{5(CaS)}$$
$$+ \underset{\text{Lime.}}{2(CaO)} + \underset{\text{Carbonic anhydride.}}{2(CO^2)}$$

The process we have just described is known as Leblanc's.

The carbonate of sodium thus furnished is not pure: in order to render it so a concentrated solution is made, which is submitted to the action of a current of carbonic gas. The impurities remain dissolved, and the greater part of the alkaline salt is deposited in the state of very pure bicarbonate, answering to the formula $\left(CO''\left\{\begin{matrix}ONa\\OH\end{matrix}\right.\right)$, which is produced by a reaction analogous to that described when speaking of bicarbonate of potassium.

Bicarbonate of sodium when gently heated loses carbonic anhydride and water, and leaves a residue of very pure neutral carbonate, as the following equation shows:—

$$\underset{\text{Bicarbonate of sodium.}}{2\left(CO''\left\{\begin{matrix}ONa\\OH\end{matrix}\right.\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Carbonic anhydride.}}{\left(CO^2\right)} + \underset{\text{Carbonate of sodium.}}{\left(CO''\left\{\begin{matrix}ONa\\ONa\end{matrix}\right.\right)}$$

Carbonate of sodium is insoluble in alcohol; 100 parts of water at 10° dissolve 12·1 of the salt; 51·7 at 38°, and 45·5 at 104°. The solubility of this salt, like that of sulphate of sodium, augments first, and decreases afterwards as the temperature is raised.*

Carbonate of sodium crystallized at the ordinary temperature contains 10 molecules of water of crystallization; its formula is $\left(CO''\left\{\begin{matrix}ONa\\ONa\end{matrix}\right. + 10\ aq.\right)$. It is efflorescent, and when heated, first undergoes aqueous, and afterwards igneous fusion.

**Bicarbonate of Sodium** $\left(CO''\left\{\begin{matrix}ONa\\OH\end{matrix}\right.\right)$.—We have seen how this salt is prepared; it exists naturally in the Vichy waters, and is used in medicine.

**Sesquicarbonate of Sodium.**—Certain lakes in Hungary and America contain a carbonate of sodium known under the name of *natron* or salt of *trona*, and which has for formula

$$\left(CO''\left\{\begin{matrix}ONa\\ONa\end{matrix}\right.\right)^2, \left(CO''\left\{\begin{matrix}ONa\\OH\end{matrix}\right.\right) + 2\ aq.$$

**Hydrate of Sodium** $\left(\left.\begin{matrix}Na\\H\end{matrix}\right\}O\right)$.—Hydrate of sodium is prepared by means of the carbonate, like hydrate of potassium. It is a powerful base, having the same properties and the same uses as hydrate of potassium.

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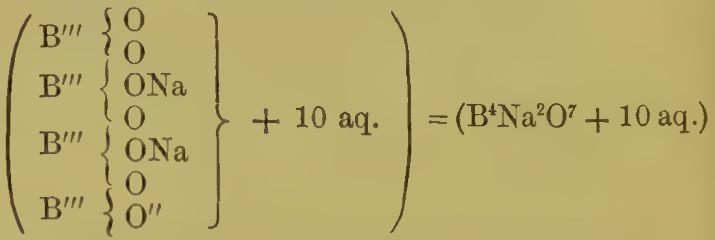
* These numbers are applied to the carbonates supposed to be anhydrous.

**Nitrate of Sodium** $\left(\left.\begin{array}{l}\mathrm{NO^2}\\\mathrm{Na}\end{array}\right\}\mathrm{O}\right)$.—Nitrate of sodium (cubic nitre) is formed in considerable beds in Peru. It crystallizes in transparent rhombohedral prisms; it has a cooling saline taste, and is somewhat deliquescent, which prevents it being powdered; 100 parts of water dissolve 23 p. at 10°, and 218·5 at 119°; it is soluble in alcohol, and its properties are similar to those of nitrate of potassium.

It is used in the manufacture of saltpetre and nitric acid.

**Borate of Sodium**



$$\left(\left.\begin{array}{ll}\mathrm{B'''} & \left\{\begin{array}{l}\mathrm{O}\\\mathrm{O}\end{array}\right.\\ \mathrm{B'''} & \left\{\begin{array}{l}\mathrm{ONa}\\\mathrm{O}\end{array}\right.\\ \mathrm{B'''} & \left\{\begin{array}{l}\mathrm{ONa}\\\mathrm{O}\end{array}\right.\\ \mathrm{B'''} & \left\{\mathrm{O''}\right.\end{array}\right\} + 10\ \mathrm{aq.}\right) = (\mathrm{B^4Na^2O^7} + 10\ \mathrm{aq.})$$

Formerly the borax used in Europe was procured from the evaporation of the water of certain lakes in Asia. It was known as tincal, corresponded to the above formula, and was presented under the form of prisms.

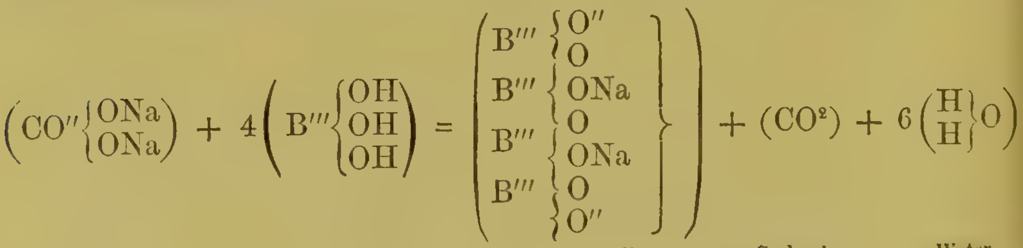
Borax is now prepared artificially, when it only contains five molecules of water of crystallization, and crystallizes in octahedra.

Melted borax dissolves metallic oxides, and its viscidity causing it to act as a varnish, it preserves substances with which it is heated at a high temperature, from oxidation. It is owing to this that borax preserves the surface of metals very bright, and thus renders easy the soldering of iron with copper, and gold with certain alloys.

Borax is also used in testing by the blowpipe; on dissolving metallic oxides, it assumes certain characteristic colours.

The crude borax or tincal may be obtained by repeated crystallizations. The following is the mode used to prepare artificial borax:

In a wooden vat lined with lead, and heated by steam, 1200 kilogrammes of crystallized carbonate of sodium are dissolved in a quantity of water, which, added to that arising from the condensation of the vapour, has a weight of about 2000 kilogrammes. When the solution is completed, 1000 kilogrammes of the boracic acid of Tuscany are gradually added. A strong effervescence takes place, carbonic anhydride is disengaged, and borate of sodium is formed.

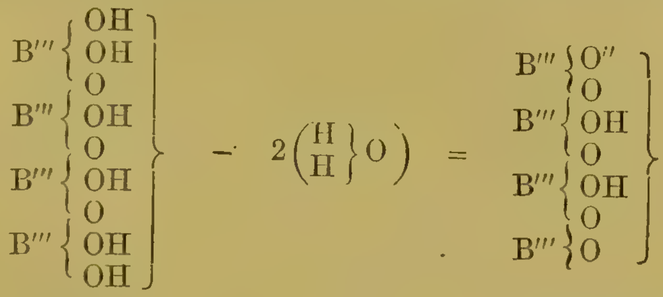


$$\left(\mathrm{CO''}\left\{\begin{array}{l}\mathrm{ONa}\\\mathrm{ONa}\end{array}\right.\right) + 4\left(\mathrm{B'''}\left\{\begin{array}{l}\mathrm{OH}\\\mathrm{OH}\\\mathrm{OH}\end{array}\right.\right) = \left(\left.\begin{array}{ll}\mathrm{B'''} & \left\{\begin{array}{l}\mathrm{O''}\\\mathrm{O}\end{array}\right.\\ \mathrm{B'''} & \left\{\mathrm{ONa}\right.\\ \mathrm{B'''} & \left\{\begin{array}{l}\mathrm{O}\\\mathrm{ONa}\end{array}\right.\\ \mathrm{B'''} & \left\{\begin{array}{l}\mathrm{O}\\\mathrm{O''}\end{array}\right.\end{array}\right\}\right) + (\mathrm{CO^2}) + 6\left(\left.\begin{array}{l}\mathrm{H}\\\mathrm{H}\end{array}\right\}\mathrm{O}\right)$$

Carbonate of sodium. Boracic acid. Borate of sodium. Carbonic anhydride. Water.

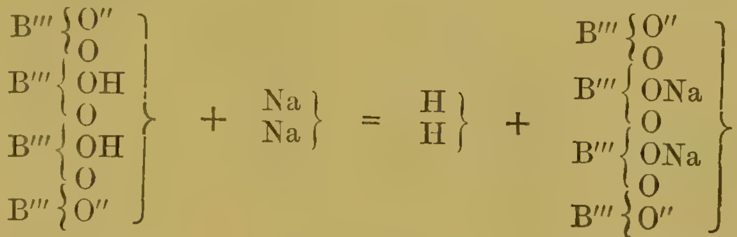
When the liquid marks 21° by Baumé's areometer, the saturation is regarded as complete; it is left to deposit during twenty-four hours; then by means of a low tap the clear liquid is drawn into shallow leaden tubs, where crystallization soon takes place: the slower the crystallization, the more voluminous are the crystals. They are in the form of prisms, and contain ten molecules of water of crystallization: this large quantity of water which the prismatic crystals of borax contain makes its carriage expensive, therefore octahedral borax is preferred, as containing only half the quantity of water. In order to obtain borax in octahedra, a solution of the salt is made, marking 30° or 32° by Baumé's areometer, and left to crystallize at a temperature of from 56° to 79°.

Borax has been improperly called borate of soda; it is really not a simple borate, but the disodic salt of the second anhydride of a tetraboracic acid.



$$\left.\begin{array}{l} B'''\left\{\begin{array}{l}OH\\OH\\O\end{array}\right.\\ B'''\left\{\begin{array}{l}OH\\O\end{array}\right.\\ B'''\left\{\begin{array}{l}OH\\O\end{array}\right.\\ B'''\left\{\begin{array}{l}OH\\OH\end{array}\right.\end{array}\right\} - 2\left(\left.\begin{array}{l}H\\H\end{array}\right\}O\right) = \left.\begin{array}{l} B'''\left\{\begin{array}{l}O''\\O\end{array}\right.\\ B'''\left\{\begin{array}{l}OH\\O\end{array}\right.\\ B'''\left\{\begin{array}{l}OH\\O\end{array}\right.\\ B'''\left\}O\right.\end{array}\right\}$$

Tetraboracic acid (unknown). Water. 2nd tetraboracic anhydride (unknown).

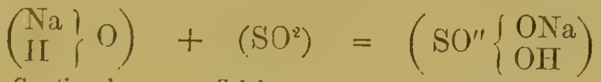


$$\left.\begin{array}{l} B'''\left\{\begin{array}{l}O''\\O\end{array}\right.\\ B'''\left\{\begin{array}{l}OH\\O\end{array}\right.\\ B'''\left\{\begin{array}{l}OH\\O\end{array}\right.\\ B'''\left\}O''\right.\end{array}\right\} + \left.\begin{array}{l}Na\\Na\end{array}\right\} = \left.\begin{array}{l}H\\H\end{array}\right\} + \left.\begin{array}{l} B'''\left\{\begin{array}{l}O''\\O\end{array}\right.\\ B'''\left\{\begin{array}{l}ONa\\O\end{array}\right.\\ B'''\left\{\begin{array}{l}ONa\\O\end{array}\right.\\ B'''\left\}O''\right.\end{array}\right\}$$

2nd anhydride of tetraboracic acid (unknown). Sodium. Hydrogen. Disodic salt of the 2nd tetraboracic anhydride (borax).

**Hyposulphite of Sodium.**—When we spoke of the acids of sulphur, we saw that this salt is obtained by boiling neutral sulphite of sodium with sulphur, filtering and crystallizing. The neutral sulphite used for this purpose may be prepared by dividing a solution of caustic soda into two parts, supersaturating one part by a current of anhydrous sulphurous acid gas, and then adding the other part.

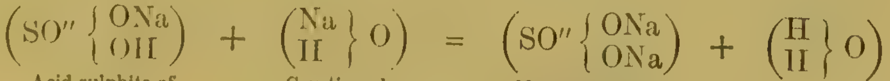
1st.



$$\left(\left.\begin{array}{l}Na\\H\end{array}\right\}O\right) + (SO^2) = \left(SO''\left\{\begin{array}{l}ONa\\OH\end{array}\right.\right)$$

Caustic soda. Sulphurous anhydride. Acid sulphite of sodium.

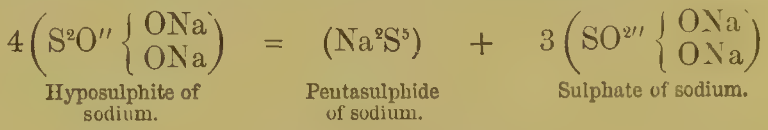
2nd.



$$\left(SO''\left\{\begin{array}{l}ONa\\OH\end{array}\right.\right) + \left(\left.\begin{array}{l}Na\\H\end{array}\right\}O\right) = \left(SO''\left\{\begin{array}{l}ONa\\ONa\end{array}\right.\right) + \left(\left.\begin{array}{l}H\\H\end{array}\right\}O\right)$$

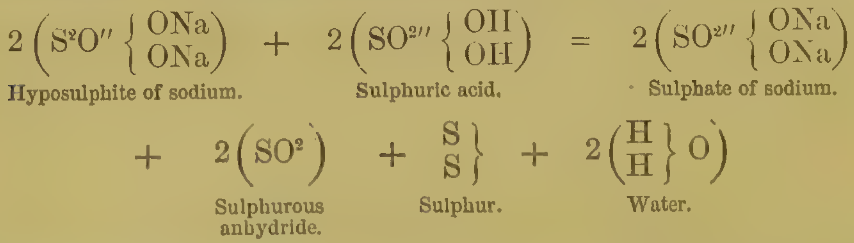
Acid sulphite of sodium. Caustic soda. Neutral sulphite of sodium. Water.

The hyposulphite of sodium crystallizes in voluminous crystals; it is bitter, and easily dissolves in water, but is insoluble in alcohol. Its crystals contain water of crystallization: under the influence of heat, it first undergoes aqueous fusion, then becomes anhydrous, and finally is converted into a mixture of sulphate and pentasulphide of sodium.



$$\underset{\text{Hyposulphite of sodium.}}{4\left(S^2O''\left\{\begin{matrix}ONa\\ONa\end{matrix}\right.\right)} = \underset{\text{Pentasulphide of sodium.}}{(Na^2S^5)} + \underset{\text{Sulphate of sodium.}}{3\left(SO^{2''}\left\{\begin{matrix}ONa\\ONa\end{matrix}\right.\right)}$$

When treated by an acid, the hyposulphite of sodium gives rise to a disengagement of sulphurous anhydride and a deposit of sulphur:



$$\underset{\text{Hyposulphite of sodium.}}{2\left(S^2O''\left\{\begin{matrix}ONa\\ONa\end{matrix}\right.\right)} + \underset{\text{Sulphuric acid.}}{2\left(SO^{2''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)} = \underset{\text{Sulphate of sodium.}}{2\left(SO^{2''}\left\{\begin{matrix}ONa\\ONa\end{matrix}\right.\right)}$$

$$+ \underset{\text{Sulphurous anhydride.}}{2\left(SO^2\right)} + \underset{\text{Sulphur.}}{\left.\begin{matrix}S\\S\end{matrix}\right\}} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

The solution of hyposulphite of sodium dissolves the chloride, bromide, and iodide of silver.

It is a powerful reducing agent.

**Hypochlorite of Sodium** ($ClNaO$).—This salt has not been obtained in a pure state, but a mixture of chloride of sodium and the hypochlorite of sodium is prepared by a similar process to that used to obtain Javelle's water. This mixture, which is called chloride of soda, or Labaraque's solution, has the same properties and the same uses as Javelle's water; it is used as a disinfectant and for bleaching.

**Characteristics of Sodic Salts.**—Sodic salts are known by the following characters:

1st. Like the salts of potash, their solutions are not precipitated by alkaline carbonates.

2nd. The sulphate crystallizes with water of crystallization, and is efflorescent; it is the same with the carbonate.

3rd. Bichloride of platinum does not precipitate the salts of soda, even in presence of alcohol, notwithstanding Orfila's assertions to the contrary, who must have operated with impure reagents, or on solutions extremely concentrated.

4th. The salts of soda are not precipitated by tartaric, perchloric or hydrofluosilicic acids.

5th. They give a white crystalline precipitate with the bimetantimoniate of potassium. This reagent ought to be washed before being employed, that it may not contain alkali in excess, otherwise the precipitate will not form for a long time.

6th. Periodic acid also gives a precipitate of periodate of sodium $(INaO^4)^2, (Na^2O)$ with the concentrated solutions of salts of soda.

## LITHIUM, RUBIDIUM, CESIUM.

These three metals are of too little importance of themselves to be studied in a work like this. We will only say a few words concerning the analytic method which caused MM. Bunsen and Kirchoff to suspect the existence of the two latter, and which guided them in the operations they devised to isolate these metals. This method has received the name of spectrum analysis.

We know that when a luminous ray is decomposed by a prism, the different colours of the rainbow are obtained. To these colours united, the name of spectrum is given.

When a volatile metallic compound, a chloride for instance, is placed in the flame of a taper, the spectrum of this flame is transformed, and different coloured rays are observed. The colour and the disposition of the rays produced by a metal being always the same, the spectra of the different metals have been determined by experiments. Therefore, by examining the spectrum which a given substance furnishes, it is possible to know the metals it contains.

M. Bunsen and M. Kirchoff having found in the spectrum furnished by the residue of the evaporation of certain mineral waters, rays which do not belong to any known metal, suspected the existence of one or two new ones, and they were able to isolate cesium and rubidium.

In the experiments which they performed for the separation of these bodies the spectrum still served as guide. When they submitted their matter to reactions which divided the substances contained in it into different groups, the spectrum indicated in which of these groups the body sought for was to be found.

Rubidium and cesium have properties much resembling those of potassium, but they are more electro-positive than potassium.

## SILVER $\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}$

Atomic weight = 108.* Molecular weight = 216.

Silver is found native, but in too small quantity to be sufficient for the amount required. The metal is generally extracted from its sulphide.

The metallurgic operations which this extraction necessitates are too complicated for us to speak of them in detail. Sulphide of silver is transformed into double chloride of silver and sodium, on which mercury is made to act. The mercury then assumes the state of chloride, and liberates silver, with which it forms an amalgam, and the silver is extracted from this amalgam by distillation. Sometimes the silver is precipitated from its chloride by iron, and the mass is then agitated with mercury, in order to produce the amalgamation.

* 107·93 according to M. Stas' latest researches.

In the first of these processes, which is the American method, the amalgamation and the reduction go on together, and the operation is conducted in the cold; in the second, which is practised at Freyberg in Germany, the amalgamation and the reduction are two separate operations, and the chlorination takes place by the aid of heat.

Silver appears to be white, though it assumes a yellow colour when a ray of light is reflected several times from its surface. It has a remarkable lustre, and, with the exception of gold, is the most malleable of all metals; it is also very ductile and has great tenacity. It fuses at about 1000° centigrade. When slowly cooled after melting, it crystallizes in large octahedra. It may be distilled by means of the oxyhydrogen blow-pipe; its vapours assume a green colour.

The density of silver is 10·4743.

Melted silver absorbs oxygen, which is disengaged as the temperature is lowered. This is a simple solution of oxygen in the liquid silver, and not a combination; if the silver be slightly alloyed with gold or copper, it loses this property.

Silver is naturally soft, but it acquires hardness when alloyed with copper. For this reason, it is combined with small quantities of this metal, in the arts, in order to work it with greater ease. The proportions of copper which may be added to silver are fixed by law. In England, the coinage (standard silver) contains 7·5 per cent. of copper, in France it contains 10 per cent.

Silver oxidizes neither in cold nor hot air, but the presence of ozone causes it to oxidize.

Hydrosulphuric acid blackens silver, and in this case a sulphide of silver and hydrogen are produced.

$$\underset{\text{Silver.}}{\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}} + \underset{\text{Hydrosulphuric acid.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}S\right)} = \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}} + \underset{\text{Sulphide of silver.}}{\left(\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}S\right)}$$

Sulphuric acid does not act on silver unless it be concentrated and boiling, when sulphurous anhydride and sulphate of silver are produced.

$$\underset{\text{Sulphuric acid.}}{2\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Silver.}}{\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}} = \underset{\text{Sulphate of silver.}}{\left(\left.\begin{matrix}SO^{2''}\\Ag^2\end{matrix}\right\}O^2\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Sulphurous anhydride.}}{(SO^2)}$$

Nitric acid acts on silver when cold, and still more so when hot, producing nitrate of silver and binoxide of nitrogen.

$$\underset{\text{Nitric acid.}}{8\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)} + \underset{\text{Silver.}}{3\left(\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}\right)} = \underset{\text{Nitrate of silver.}}{6\left(\left.\begin{matrix}NO^2\\Ag\end{matrix}\right\}O\right)}$$

$$+ \underset{\text{Water.}}{4\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Binoxide of nitrogen.}}{2\,(NO)}$$

At a red heat silver decomposes hydrochloric acid, forming chloride of silver, and liberating hydrogen:

$$\begin{array}{ccccccc} \left.\begin{matrix}Ag\\Ag\end{matrix}\right\} & + & 2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right) & = & \left.\begin{matrix}H\\H\end{matrix}\right\} & + & 2\left(\left.\begin{matrix}Ag\\Cl\end{matrix}\right\}\right) \\ \text{Silver.} & & \text{Hydrochloric acid.} & & \text{Hydrogen.} & & \text{Chloride of silver.} \end{array}$$

The prolonged contact of silver with a solution of chloride of sodium gives rise to the formation of a certain quantity of double chloride of silver and sodium, which dissolves, and the liquid becomes alkaline.

### COMBINATIONS OF SILVER WITH MONATOMIC METALLOIDS.

Silver forms a single compound with each of these bodies. The chloride, bromide, iodide, and fluoride of silver are known.

**Chloride of Silver.**—Chloride of silver is found native crystallized in octahedra; as it is insoluble, it may be easily obtained by precipitating the solution of a salt of silver by hydrochloric acid, or by a soluble chloride.

$$\begin{array}{ccccccc} \left(\left.\begin{matrix}NO^2\\Ag\end{matrix}\right\}O\right) & + & \left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right) & = & \left(\left.\begin{matrix}Ag\\Cl\end{matrix}\right\}\right) & + & \left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right) \\ \text{Nitrate of silver.} & & \text{Hydrochloric acid.} & & \text{Chloride of silver.} & & \text{Nitric acid.} \end{array}$$

The chloride of silver then forms a white flocculent mass.

Chloride of silver is absolutely insoluble in pure water. At 10° salt water dissolves the $\frac{17}{10000}$ of the weight of the salt it contains, at 18° $\frac{24}{10000}$, at 100° $\frac{40}{10000}$, at 0° scarcely any.

Chloride of silver easily dissolves in hyposulphite of sodium, in cyanide of potassium, and in ammonia; hydrochloric acid also dissolves it, but in very small quantity.

On evaporating its ammoniacal or hydrochloric solution, chloride of ilver crystallizes in octahedra, which are identical with the native rystals.

The chemical rays of the spectrum act strongly on chloride of silver: n the direct rays of the sun this salt immediately becomes violet; in liffused light, the colouring is not observed so soon; in red or yellow ights, which do not contain the chemical rays, the chloride of silver emains white, as it also does in darkness. It melts at 260°; on cooling it becomes horny, and is so soft as to be cut with a knife: its appearance causes it to be called *horn silver*. At a very high temperature t emits vapours.

Nascent hydrogen reduces the chloride of silver when cold, and free ydrogen reduces it when hot; in the latter case, however, some traces f the chloride always escape the reducing action, as M. Lieben has scertained, which causes all the analytic processes founded on this eduction to be incorrect.

When it is not melted, it is reduced by iron and zinc. If a small heap of moist chloride of silver be made, and an iron bar be placed in the centre, the reduction gradually proceeds from the centre to the exterior. Mercury also reduces chloride of silver, and the protochloride of copper possesses the same property.

$$\underset{\text{Protochloride of copper.}}{(Cu^2Cl^2)} + \underset{\text{Chloride of silver.}}{2(AgCl)} = \underset{\text{Bichloride of silver.}}{2(CuCl^2)} + \underset{\text{Silver.}}{\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}}$$

When chloride of silver is boiled with a concentrated solution of potash, oxide of silver is formed; and if sugar be added to the solution, silver is obtained in a very pure state.

Heated to a white heat with carbonate of potassium and sea salt, the chloride of silver is reduced, and furnishes a button of metallic silver. The marine salt renders the dross easier to be separated.

$$\underset{\text{Chloride of silver.}}{4\left(\left.\begin{matrix}Ag\\Cl\end{matrix}\right\}\right)} + \underset{\text{Carbonate of potassium.}}{2\left(\left.\begin{matrix}CO''\\K^2\end{matrix}\right\}O^2\right)} =$$

$$\underset{\text{Carbonic anhydride.}}{2(CO^2)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} + \underset{\text{Silver.}}{2\left(\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}\right)} + \underset{\text{Chloride of potassium.}}{4\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)}$$

The metallic sulphides, especially those of the electro-positive metals, enter into double decomposition with chloride of silver.

**Bromide of Silver** $\left(\left.\begin{matrix}Ag\\Br\end{matrix}\right\}\right)$.—Bromide of silver is found in the native state, and may be obtained by the same processes as the chloride, with which nearly all its properties are analogous; it is distinguished from the chloride by being less soluble in ammonia, and by the action light exercises on it. When prepared in an artificial light it is white, but, if exposed to diffused daylight, it immediately becomes yellowish, and retains this tint without altering, to whatever intensity of light it may afterwards be exposed.

It may be obtained crystallized as a solid with twenty-four sides derived from the octahedron, but only by the action of hydrobromic acid on powdered silver; it does not crystallize by the spontaneous evaporation of its solution in ammonia.

**Iodide of Silver** $\left.\begin{matrix}Ag\\I\end{matrix}\right\}$.—Iodide of silver is prepared like the chloride and bromide, and, like them, exists in the native state; it is slightly soluble in ammonia; light easily alters it, changing it from the yellowish tint which is its natural colour, first to dark brown, then to black.

On causing hydriodic acid to act on finely-powdered silver, iodide of silver is obtained crystallized in dodecahedral prisms.

## COMBINATIONS OF SILVER WITH BIATOMIC METALLOIDS.

With sulphur, silver forms only one sulphide, answering to the formula ($Ag^2S$); it forms three compounds with oxygen; the suboxide ($Ag^4O$), the protoxide ($Ag^2O$), and the binoxide ($Ag^2O^2$): of these three, the protoxide alone possesses any importance.

**Sulphide of Silver** $\left(\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}S\right)$.—Sulphide of silver is found native, crystallized in the cubic system. It is the principal ore of silver. It is obtained artificially by precipitating a salt of silver by hydrosulphuric acid:

$$2\left(\left.\begin{matrix}NO^2\\Ag\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}S\right) = 2\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}S\right)$$

Nitrate of silver. Hydrosulphuric acid. Nitric acid. Sulphide of silver.

Sulphide of silver is black, and when melted or highly heated it assumes a metallic appearance. The native sulphide always has this latter aspect. Its density is 7·2.

When roasted, the sulphide of silver loses sulphurous anhydride, and leaves metallic silver; roasted with sea salt, it passes to the state of chloride, as it also does when left for some time with bichloride of copper.

**Protoxide of Silver** $\left(\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}O\right)$.—This oxide is obtained as a heavy brown powder when a salt of silver is precipitated by hydrate of sodium or potassium. In this case a hydrate $\left(\left.\begin{matrix}Ag\\H\end{matrix}\right\}O\right)$ ought to be produced; but this hydrate not being stable, the protoxide is formed.

$$2\left(\left.\begin{matrix}NO^2\\Ag\end{matrix}\right\}O\right) + 2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right) =$$

Nitrate of silver. Potassic hydrate.

$$2\left(\left.\begin{matrix}NO^2\\K\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

Nitrate of potassium. Protoxide of silver. Water.

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Oxide of silver is easily decomposed into oxygen and metallic silver when heated. It is a powerful basic anhydride, and dissolves in acids, orming well-defined salts. Water dissolves $\frac{1}{3000}$, sufficient to decom-ose the soluble haloid salts and the phosphates.

When oxide of silver is digested with ammonia, a detonating com-ound is formed, the formula of which is not definitely fixed. Some hemists consider this body (fulminating silver) as answering to the ormula $\left(\left.\begin{matrix}Ag\\H\\H\end{matrix}\right\}N\right)$, others believe that it is a triargentic nitride $\left(\left.\begin{matrix}Ag\\Ag\\Ag\end{matrix}\right\}N\right)$.

**Nitrate of Silver** $\left(\left.\begin{matrix}\mathrm{NO^2}\\ \mathrm{Ag}\end{matrix}\right\}\mathrm{O}\right)$.—Nitrate of silver is prepared by dissolving silver in boiling nitric acid. If the silver employed be pure, so is the nitrate; if the silver contain copper, like money or jewellery, the nitrate of silver is mixed with nitrate of copper. The best method of purifying it then consists in evaporating it to dryness, and melting the residue, taking care to keep it melted for some time. The nitrate of copper is decomposed into oxide of copper and volatile products; and if the temperature is not too high, the greatest part of the nitrate of silver remains intact: occasionally a small portion of the mass is taken out with a rod and dissolved in water, which is filtered, and ammonia is added. So long as the reagent produces a blue tint there remains some nitrate of copper intact; when the ammonia no longer acts, the decomposition of this salt is complete.

The mass when cold is dissolved in water, filtered to separate the oxide of copper, and evaporated to the consistence of a thick syrup; the nitrate of silver crystallizes when the liquid cools. It may then be evaporated to dryness, the salt melted, and poured in layers on to porcelain plates, or formed into sticks in small moulds of cast iron; in this latter form it is employed as an escharotic by surgeons, and is called lunar caustic.

Instead of decomposing nitrate of copper in the manner just described, it is more simple to treat the mixture of the two salts by a soluble chloride, which precipitates the silver only in the state of chloride. This chloride is well washed and dried, and then heated to white redness in a crucible, after having been mixed with carbonate of potassium and sea salt; a sediment of very pure silver is extracted from the crucible, the latter being broken on cooling. This sediment, dissolved in nitric acid, forms very pure nitrate of silver.

Nitrate of silver crystallizes in beautiful transparent rhomboid laminæ, especially on evaporating its acid solutions. When melted, it appears as a white mass of crystalline structure.

As nitrate of silver is decomposed by heat, giving metallic silver, it becomes black after repeated fusions.

When this salt is poured into sticks there is always some residue, which is melted a second, and sometimes a third time; this residue then assumes the colour often observed in lunar caustic.

The solution of nitrate of silver is decomposed by hydrogen, as it would be by a metal such as zinc, nitric acid is formed, and silver is deposited.

$$\underset{\text{Nitrate of silver.}}{2\left(\left.\begin{matrix}\mathrm{NO^2}\\ \mathrm{Ag}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}} = \underset{\text{Nitric acid.}}{2\left(\left.\begin{matrix}\mathrm{NO^2}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Silver.}}{\left.\begin{matrix}\mathrm{Ag}\\ \mathrm{Ag}\end{matrix}\right\}}$$

Nitrate of silver is decomposed by organic substances under the influence of light. It stains the skin black, and is used for marking linen and dyeing hair; the stains on the skin disappear if washed immediately with a solution of potassic cyanide. As to the writing on linen, said to be indelible, if submitted to the action of chlorine solution until it become white, and then washed first with pure water and then with solution of ammonia, it will disappear.

Nitrate of silver is given internally in epilepsy. But invalids who take it ought to be kept in the dark, or their skin will become bronzed. It is, however, an uncertain remedy.

**Characteristics of Salts of Silver.**—The soluble salts of silver are recognized by the following properties.

1st. They are always colourless when no elements of a coloured acid enter into their composition, and they generally blacken when exposed to the light.

2nd. Hydrochloric acid and the soluble chlorides produce in their solutions a white flocculent precipitate of chloride of silver which is not acted on by acids, but which dissolves readily in ammonia, cyanide of potassium, and hyposulphite of sodium; this precipitate assumes a violet tint when exposed to the light.

3rd. The soluble phosphates and arsenites cause in the above solutions the formation of a clear yellow precipitate of phosphate or arsenite of silver, soluble in ammonia and in acid liquids.

4th. Arseniates produce therein a brick-red precipitate of arseniate of silver.

5th. Sulphuretted hydrogen forms a black precipitate of sulphide of silver, which is insoluble in the hydrosulphate of ammonia, but which nitric acid easily transforms into nitrate of silver.

6th. Fixed alkalies in presence of salts of silver give a brown precipitate of oxide of silver, which, when brought into contact with ammonia, becomes black, and acquires explosive properties.

7th. Soluble iodides transform soluble salts of silver into iodide of silver which is precipitated.

This iodide is yellowish, easily affected by light, almost insoluble in ammonia, but easily dissolved in hyposulphite of sodium and in cyanide of potassium. Boiling nitric acid slowly decomposes it, forming nitrate of silver, and disengaging violet vapours of iodine.

## APPENDIX TO MONATOMIC METALS.

**Ammoniacal Compounds.**—We have seen when speaking of ammonia that the residue ($NH^4$) (ammonium) can act as a monatomic metal; the compounds of this radicle are numerous; the most important and the only ones we will study are:

The monosulphide and the hydrosulphate of ammonium.
The chloride of ammonium.
The sulphate of ammonium.
The nitrate of ammonium.
The carbonate of ammonium.

**Monosulphide and Hydrosulphate of Ammonium.** — When two volumes of hydrosulphuric acid and four volumes of very dry ammoniacal gas are mixed at a low temperature, a very unstable crystallized body is produced, which is the monosulphide of ammonium $\left(\left.\begin{matrix}NH^4\\NH^4\end{matrix}\right\}S\right)$. If, on the contrary, equal volumes of these two gases be mixed, a very volatile yellow product would be obtained, which is the hydrosulphate of ammonium $\left(\left.\begin{matrix}NH^4\\H\end{matrix}\right\}S\right)$.

These compounds are only employed in aqueous solution: to prepare them we dilute ammonia with water, and supersaturate with hydrosulphuric acid; thus hydrosulphate of ammonium is formed.

$$\underset{\text{Hydrosulphuric acid.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}S\right)} + \underset{\text{Ammonia.}}{\left(NH^3\right)} = \underset{\text{Hydrosulphate of ammonium.}}{\left(\left.\begin{matrix}NH^4\\H\end{matrix}\right\}S\right)}$$

If a quantity of ammonia, equal to that used to prepare it, be added to this hydrosulphate, it becomes transformed into monosulphide.

$$\underset{\text{Hydrosulphate of ammonium.}}{\left(\left.\begin{matrix}NH^4\\H\end{matrix}\right\}S\right)} + \underset{\text{Ammonia.}}{\left(NH^3\right)} = \underset{\text{Monosulphide of ammonium.}}{\left(\left.\begin{matrix}NH^4\\NH^4\end{matrix}\right\}S\right)}$$

These sulphides possess the property of precipitating the greater part of metallic solutions, and for this reason they are much used in mineral analysis.

**Chloride of Ammonium** $\left(\left.\begin{matrix}NH^4\\Cl\end{matrix}\right\}\right)$.—Ammoniacal gas and hydrochloric acid unite in equal volumes to constitute chloride of ammonium.

$$\underset{\text{Ammonia.}}{\left(NH^3\right)} + \underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\text{Chloride of ammonium.}}{\left(\left.\begin{matrix}NH^4\\Cl\end{matrix}\right\}\right)}$$

But the salt is not generally obtained in this way. Formerly it was prepared by heating in glass vessels the soot arising from the combustion of camel's dung; the chloride of ammonium was volatilized, and was deposited on the upper parts of the vessels which were cold; it was then extracted by breaking the vessels.

Chloride of ammonium is at present prepared by saturating with hydrochloric acid the waters condensed in coal-gas works, those which arise from the distillation of animal matter and the urine arising from night soil. All these matters contain carbonate or hydrosulphate of ammonium.

When hydrochloric acid is too expensive, these waters are treated by the sulphate of calcium; double decomposition takes place, carbonate of calcium is precipitated, and sulphate of ammonium remains dissolved.

The solution of this new salt is decanted, concentrated to 19° or 20° (Baumé), chloride of sodium is added, and it is boiled; a second decomposition is produced: sulphate of sodium and chloride of ammonium are formed, and the greater part of the sulphate is deposited during the boiling. When this salt ceases to be deposited, the solution is allowed to cool; and, as then the solubility of the chloride of ammonium decreases, while that of the sulphate of sodium augments up to 33°, the chloride of ammonium is alone deposited.

The salt thus obtained is then sublimed and made ready for sale. The chloride of ammonium, known in commerce as sal-ammoniac, crystallizes in small octahedra, which are entangled together, so as to resemble flexible needles.

When heated it volatilizes without melting, unless it be submitted to a pressure greater than that of the atmosphere. Alcohol dissolves it very sparingly, but it dissolves in about its own weight of boiling water, and in 2·7 parts of cold water, of which it lowers the temperature in dissolving.

Alkaline oxides and alkaline earths decompose the chloride of ammonium, ammonia is disengaged, and a metallic chloride is formed:

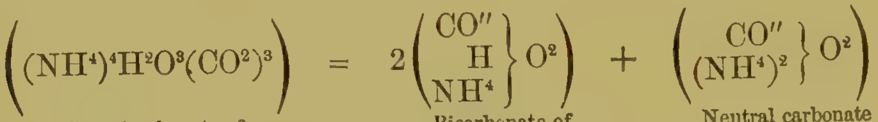
$$\underset{\text{Chloride of ammonium.}}{2\left(\left.\begin{matrix}\mathrm{NH^4}\\ \mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\text{Oxide of calcium.}}{(\mathrm{Ca''O})} = \underset{\text{Chloride of calcium.}}{(\mathrm{CaCl^2})} + \underset{\text{Ammonia.}}{(\mathrm{NH^3})}$$

**Sulphate of Ammonium** $\left(\mathrm{SO^{2''}}\left\{\begin{matrix}\mathrm{ONH^4}\\ \mathrm{ONH^4}\end{matrix}\right.\right)$.—We have seen how this salt is manufactured on a large scale: it is purified by gentle roasting to destroy the organic matters with which it is mixed, and recrystallizing. The sulphate of ammonium is presented in colourless crystals, which are isomorphous with those of sulphate of potassium; it dissolves in two parts of cold or one of boiling water; it resists a temperature of 180° without decomposing; but, if heated sufficiently, it is entirely transformed into volatile products: sulphate of ammonium, being the cheapest of the ammoniacal salts, promises to become important in agriculture as a source of nitrogen.

**Carbonates of Ammonium.**—Carbonate of ammonium is obtained by heating in a cast-iron retort a mixture of chalk (carbonate of lime) and sulphate of ammonium; the carbonate of ammonium, which is volatile, becomes condensed in the cold parts of the apparatus. It presents the appearance of a white translucent mass with a fibrous texture; it has a fresh ammoniacal odour, and presents an alkaline reaction.

A solution of this salt supersaturated with carbonic anhydride deposits crystals of bicarbonate, which are not affected by air, and which have for formula $\left(\left.\begin{matrix}\mathrm{CO''}\\ \mathrm{NH^4}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O^2}\right)$.

If, instead of treating the solution of the carbonate of ammonium of commerce by concentrated carbonic anhydride, it be saturated by concentrated ammonia, the liquor deposits crystals of volatile sesquicarbonate of ammonia. These crystals answer to the formula $((CO^2)^3(NH^4)^4H^2O^3)$. As it is difficult to conceive how such a molecule can be constituted, there is reason to believe that the sesquicarbonate of ammonia is not a real atomic compound, but that it is formed by the union of two molecules of bicarbonate of ammonium with one of neutral carbonate.



$$\left((NH^4)^4H^2O^3(CO^2)^3\right) = 2\left(\left.\begin{matrix}CO''\\H\\NH^4\end{matrix}\right\}O^2\right) + \left(\left.\begin{matrix}CO''\\(NH^4)^2\end{matrix}\right\}O^2\right)$$

Sesquicarbonate of ammonium. Bicarbonate of ammonium. Neutral carbonate of ammonium.

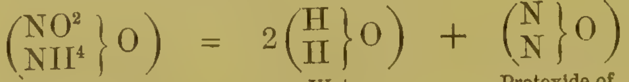
The neutral carbonate of ammonium is not known in a free state.

The carbonate of commerce appears to be constituted by a mixture of bicarbonate and sesquicarbonate, or rather by a mixture of acid and neutral carbonates, containing more of the acid carbonate than the salt known as the sesquicarbonate.

**Nitrate of Ammonium** $\left(\left.\begin{matrix}NO^2\\NH^4\end{matrix}\right\}O\right)$.—This salt is obtained by saturating ammonia or carbonate of ammonium by nitric acid, and slowly evaporating the solution.

Nitrate of ammonium crystallizes in hexagonal prisms similar to those of saltpetre, and containing 12 atoms of water of crystallization. This salt has a bitter acrid taste; boiling water dissolves its own weight, and cold water about half its weight; on dissolving in water it lowers the temperature considerably; alcohol does not dissolve it.

When submitted to the action of heat, nitrate of ammonium is decomposed into water and protoxide of nitrogen:



$$\left(\left.\begin{matrix}NO^2\\NH^4\end{matrix}\right\}O\right) = 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}N\\N\end{matrix}\right\}O\right)$$

Nitrate of ammonium. Water. Protoxide of nitrogen.

Nitrate of ammonium is contained in rain-water.

**Characteristics of Ammonical Salts.**—These salts are recognized by the property they possess of disengaging ammonia under the influence of bases. To show this property, a fragment of potash is thrown into a tube closed at one end, and a little of the salt to be examined, and a few drops of water are added; in the upper part of the tube, moist red litmus paper is placed and the tube is heated; if it be a salt of ammonium, ammoniacal vapour is at once disengaged and turns the litmus paper blue. Even when the salt is in small quantity, the smell of ammonia is distinctly perceptible.

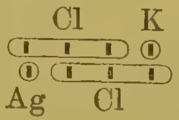
## GENERAL REMARKS ON THE MONATOMIC METALS.

Being monatomic, the metals of this group can only form a limited number of compounds, and these are sometimes instable, as we have seen is the case with hydrate of silver $\left(\left.\begin{matrix}\text{Ag}\\ \text{H}\end{matrix}\right\}\text{O}\right)$.

Besides those combinations which obey the laws of atomicity, other compounds are known which seem to form exceptions to these laws, such as the double chloride of silver and sodium (AgCl,NaCl), in which the silver is combined with three atoms, which are monatomic, like itself.

A few years ago, M. Cannizzaro enunciated the idea that such bodies are simply formed by the juxtaposition of two different molecules; that they resemble rather those into which water of crytallization enters than true atomic compounds. M. Kékulé, who has recently recurred to this idea, has proposed calling these bodies molecular combinations.

MM. Kékulé and Cannizzaro's ideas may be correct, but we have seen that the existence of double chlorides, bromides, and iodides, may be accounted for by admitting that halogen metalloids are triatomic, and that they act in these bodies with their maximum capacity for saturation. The double chloride of silver and potassium would be, according to this hypothesis, $\left(\left.\begin{matrix}\text{Ag}\\ \text{K}\end{matrix}\right\}\text{Cl}^2\right)$, and its constitution would be what the following symbolic design shows:



## SECOND CLASS (BIATOMIC METALS).

### CALCIUM Ca''.

Atomic weight = 40. Probable molecular weight = 40.

Davy obtained calcium by decomposing lime by the galvanic battery in presence of mercury, and displacing by heat the mercury of the amalgam thus produced. More recently, M. Caron isolated this metal by decomposing the chloride of calcium by sodium in presence of zinc at a high temperature. The metal is obtained alloyed with zinc, from which it is separated by submitting the alloy to the action of a very strong heat in a crucible of charcoal. The calcium thus prepared always contains a little iron; it is of a brass-yellow colour.

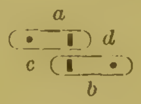
The density of calcium is 1·5778. This metal is not sensibly volatile. It oxidizes and becomes hydrated in moist air: after a certain time it is entirely transformed into slaked lime. It can be preserved in a vessel full of dry air, but becomes covered with a greyish coating which deprives it of its metallic lustre. It burns with difficulty in the flame of the blowpipe on account of the layer of oxide which immediately forms, and which preserves it from further oxidation.

Calcium is biatomic, and is therefore capable of uniting with two atoms of a monatomic element or with two residues of the same atomicity.

Combined with chlorine, bromine, iodine, or fluorine, we obtain the chloride ($Ca''Cl^2$), the bromide ($Ca''Br^2$), the iodide ($Ca''I^2$), and the fluoride ($Ca''Fl^2$); united with hydroxyl, the hydrate of calcium or slaked lime is obtained $\left(Ca''\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)$.

The two affinities of calcium may also be saturated by the two affinities of a biatomic metalloid, such as oxygen or sulphur, as in the anhydrous oxide ($CaO$) and the monosulphide ($CaS$)

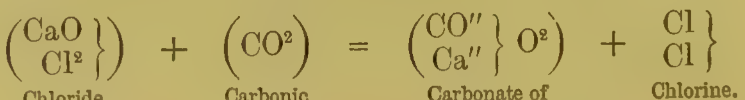
Calcium and oxygen both being biatomic, may be saturated incompletely, and give the biatomic group $CaO''$, as the following figure indicates



in which *a* represents one atom of calcium and *b* one atom of oxygen. We see that one of the two centres of attraction of the calcium is saturated by one of the centres of attraction of the oxygen, and that the group contains in *c* and *d* two non-saturated centres of attraction. I will give the radicle ($CaO$) the name of calcyl.

The oxide of calcyl ($CaO,O$), obtained by the action of oxygenized water on lime, and the bichloride of calcyl ($CaO,Cl^2$), obtained by the action of chlorine on the same body, are known.

These calcylic compounds are remarkably instable: all bodies having a tendency either to combine directly with oxide of calcium or to enter into double decomposition with it, liberate the element originally combined with this oxide. Thus on causing acids to act on binoxide of calcium, or on the chloride of calcyl, oxygen or chlorine is liberated, and a salt of lime is formed. In hygiène, this property of the chloride of calcyl (chloride of lime) is utilized to procure a constant and slow disengagement of chlorine. This compound is left in contact with the air, the carbonic anhydride seizes the oxide of calcium in order to form carbonate of calcium, and chlorine is disengaged:



$$\left(\begin{matrix}CaO\\Cl^2\end{matrix}\right\}\Bigg) + \left(CO^2\right) = \left(\begin{matrix}CO''\\Ca''\end{matrix}\right\}O^2\Bigg) + \left.\begin{matrix}Cl\\Cl\end{matrix}\right\}$$

Chloride of calcyl. Carbonic anhydride. Carbonate of calcium. Chlorine.

Before the biatomicity of calcium was known, chloride of lime was

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considered as a mixture of chloride and hypochlorite of calcium, which was written $(CaCl+CaClO)$, attributing the atomic weight 20 to calcium.

At present it is more simple to consider this body as merely a chloride of calcyl; it is nevertheless possible that it is really formed of a mixture of chloride and hypochlorite of calcium, and that its formula ought to be written $\left(CaCl^2\right)+\left(\left.\begin{matrix}Ca''\\Cl^2\end{matrix}\right\} O^2\right)$.

Instead of calcyl $(CaO)$, it is possible to have sulphocalcyl $(CaS'')$, and even radicles still more sulphuretted; thus the existence of bisulphide of calcium $(Ca''S^2) = (CaS''S)$ is explained as well as that of the pentasulphide of the same metal $(CaS^{4''}S)$.

Among the compounds formed by calcium, the most important are the oxide of calcium or lime, the chloride, the carbonate, the sulphate, and the phosphates of calcium.

**Chloride of Calcium** $(Ca''Cl^2)$.—This body is obtained by dissolving white marble in pure hydrochloric acid, evaporating the liquid to dryness, melting the residue in a crucible, and pouring it on to a marble slab. As soon as the chloride of calcium is solidified, it is powdered and placed in bottles while still hot, that it may not become moist. The chloride of calcium then appears in white layers.

If the solution of this salt be evaporated to dryness, and the salt be dried without melting, it will assume a spongy appearance.

If again a solution of chloride of calcium, concentrated by heat, be left to cool, the salt would crystallize in six-sided prisms terminated by pyramids with six faces; these crystals are hydrates, and their formula is $\left(Ca''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right. + 6\text{ aq.}\right)$.

Chloride of calcium is anhydrous when melted or simply dried; it dissolves in water, disengaging a large quantity of heat, and is very deliquescent. It is used to dry gases as well as liquids in which it does not dissolve. The spongy chloride is preferred for gases, and melted chloride for liquids.

**Carbonate of Calcium.**—This substance abounds in nature, where it exists either crystallized or amorphous, and in very variable degrees of aggregation. Marble, Aragonite, Iceland spar, chalk, limestone, calcareous marl, oolite, etc., are all constituted of carbonate of lime.

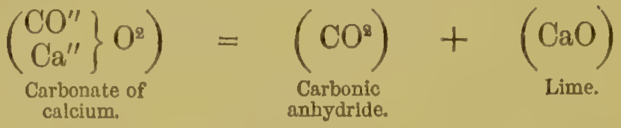
Carbonate of calcium decomposes before melting, unless the carbonic anhydride be prevented from being disengaged; in this latter case it melts, and crystallizes on cooling: the substance which is formed is identical with marble, and may even be veined by adding different oxides.

Carbonate of calcium is white and is almost insoluble in pure water. According to M. Peligot, this liquid would dissolve grm. 0·02 per litre. It dissolves in water charged with carbonic anhydride, and then passes to the state of bicarbonate. On boiling this solution, the neutral carbonate is precipitated and carbonic anhydride is disengaged. This property explains why certain waters produce calcareous incrustations, and the stalagmites and stalactites so often met with in caverns, etc., etc.

Carbonate of calcium is bimorphous. Iceland spar and Aragonite represent two varieties of this body crystallized in two different systems.

On causing different acids to act on carbonate of calcium, a calcic salt is obtained corresponding to the acid used, and carbonic anhydride is disengaged.

**Oxide of Calcium** (*Lime*).—Lime is prepared by calcining the carbonate to full redness.



$$\underset{\text{Carbonate of calcium.}}{\left(\begin{matrix}CO''\\ Ca''\end{matrix}\right\} O^2\Big)} = \underset{\text{Carbonic anhydride.}}{\left(CO^2\right)} + \underset{\text{Lime.}}{\left(CaO\right)}$$

In presence of water, lime swells up and crumbles, disengaging a great amount of heat; it is then transformed into hydrate of calcium $\left(\begin{matrix}Ca''\\ H^2\end{matrix}\right\} O^2\Big)$. Under the influence of red heat, this hydrate loses a molecule of water and returns to the state of anhydrous lime ($Ca''O$). This hydrate of calcium is called slaked lime.

Lime is white and infusible at the highest temperatures; water dissolves it sparingly, and its solubility is less in hot than in cold water: 1 part of lime requires for its solution 778 parts of water at 15°, and 1270 parts at 100°.

A solution of sugar dissolves a great quantity of lime; if alcohol be added to the solution, a compound of lime and sugar is deposited. The solution of saccharate of lime is also coagulated by heat.

It is generally supposed that lime heated to dull redness favours the decomposition of ammoniacal gas; but M. Bouis has discovered that there is no foundation for this assertion.

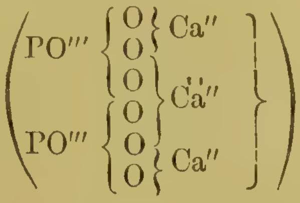
Lime exposed to air is transformed into a very hard carbonate. When mixed with siliceous matters, such as quartz sand, and even with matter that is not siliceous, such as dolomite (double carbonate of lime and magnesia), it forms mortars.

Lime containing clay (silicate of alumina) hardens under water. It is such mixtures that constitute hydraulic limes and cements. These latter contain more of the clay than the hydraulic limes. When, without containing clay, lime contains foreign substances, such as magnesia, it no longer swells so readily in presence of water, and it is then called poor lime, in contradistinction to the purest lime of commerce, which is called rich or strong lime.

In the laboratory, pure lime is obtained by decomposing pure calcareous bodies, such as white statuary marble, by heat. Nevertheless, it is generally necessary to submit the lime thus prepared to washing in distilled water, in order to free it from a small quantity of chloride.

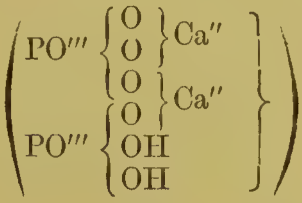
**Phosphates of Calcium.**—Three phosphates of calcium are known:—

A neutral phosphate . .



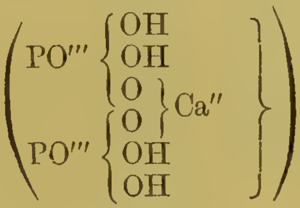
$$\left(\begin{array}{l}\mathrm{PO'''}\left\{\begin{array}{l}\left.\begin{array}{l}\mathrm{O}\\ \mathrm{O}\end{array}\right\}\mathrm{Ca''}\\ \mathrm{O}\end{array}\right.\\ \qquad\qquad\quad\}\mathrm{Ca''}\\ \mathrm{PO'''}\left\{\begin{array}{l}\mathrm{O}\\ \left.\begin{array}{l}\mathrm{O}\\ \mathrm{O}\end{array}\right\}\mathrm{Ca''}\end{array}\right.\end{array}\right)$$

An acid phosphate . .



$$\left(\begin{array}{l}\mathrm{PO'''}\left\{\begin{array}{l}\left.\begin{array}{l}\mathrm{O}\\ \mathrm{O}\end{array}\right\}\mathrm{Ca''}\\ \mathrm{O}\end{array}\right.\\ \qquad\qquad\quad\}\mathrm{Ca''}\\ \mathrm{PO'''}\left\{\begin{array}{l}\mathrm{O}\\ \mathrm{OH}\\ \mathrm{OH}\end{array}\right.\end{array}\right)$$

And a biacid phosphate .



$$\left(\begin{array}{l}\mathrm{PO'''}\left\{\begin{array}{l}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{O}\end{array}\right.\\ \qquad\qquad\quad\}\mathrm{Ca''}\\ \mathrm{PO'''}\left\{\begin{array}{l}\mathrm{O}\\ \mathrm{OH}\\ \mathrm{OH}\end{array}\right.\end{array}\right)$$

**Neutral Phosphate.**—This phosphate, improperly known as basic phosphate, forms the basis of the bones of vertebrate animals; it is there united with carbonate of calcium and organic matter. Layers of this salt are found in nature; it may be obtained artificially by pouring a mixture of alkaline phosphate and ammonia into chloride of calcium, washing and drying the precipitate which forms.

Neutral phosphate of calcium is insoluble in water, but it dissolves by the assistance of carbonic anhydride therein contained. Its presence in vegetables has been attempted to be thus explained: according to M. Paul Thénard, on the contrary, vegetables absorb phosphate of ammonia and soluble salts of calcium, which then give phosphate of calcium by double decomposition.

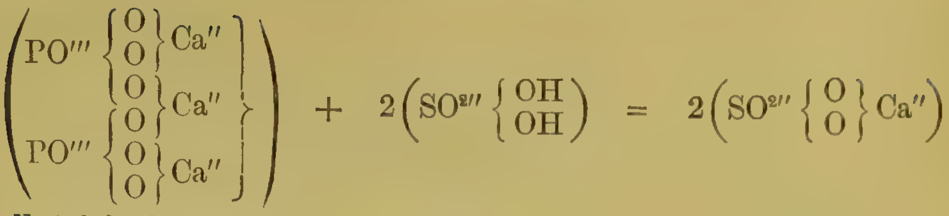
All acids cause it to pass to the state of acid phosphate.

When boiled with a solution of carbonate of sodium, it gives carbonate of calcium and phosphate of sodium.

$$\underset{\text{Neutral phosphate of calcium.}}{((\mathrm{PO'''})^2\mathrm{Ca}^3\mathrm{O}^6)} + \underset{\text{Carbonate of sodium.}}{3(\mathrm{CNa}^2\mathrm{O}^3)} = \underset{\text{Phosphate of sodium.}}{2[\mathrm{PO'''}(\mathrm{NaO})^3]} + \underset{\text{Carbonate of calcium.}}{3(\mathrm{CCaO}^3)}$$

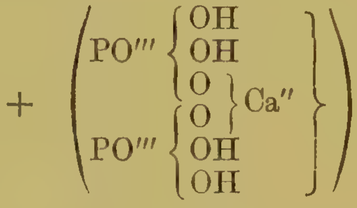
**Acid Phosphate of Calcium** $((\mathrm{PO'''})^2\mathrm{Ca}^2\mathrm{H}^2\mathrm{O}^6 + 4\ \mathrm{aq})$.—This salt is obtained by precipitating a solution of phosphate of sodium by a solution of chloride of calcium. It is improperly called neutral phosphate.

**Biacid Phosphate of Calcium** $((\mathrm{PO'''})^2\mathrm{Ca''H}^4\mathrm{O}^6)$.—This salt is obtained by treating the neutral phosphate by sulphuric acid, and adding water, which dissolves the acid phosphate and leaves the sulphate of calcium formed in the reaction.



$$\left(\begin{array}{l}\mathrm{PO}'''\left\{\begin{array}{l}\mathrm{O}\\\mathrm{O}\\\mathrm{O}\end{array}\right.\\\mathrm{PO}'''\left\{\begin{array}{l}\mathrm{O}\\\mathrm{O}\\\mathrm{O}\end{array}\right.\end{array}\left.\begin{array}{l}\left.\begin{array}{l}\mathrm{O}\\\mathrm{O}\end{array}\right\}\mathrm{Ca}''\\\left.\begin{array}{l}\mathrm{O}\\\mathrm{O}\end{array}\right\}\mathrm{Ca}''\\\left.\begin{array}{l}\mathrm{O}\\\mathrm{O}\end{array}\right\}\mathrm{Ca}''\end{array}\right\}\right)+2\left(\mathrm{SO}^{2''}\left\{\begin{array}{l}\mathrm{OH}\\\mathrm{OH}\end{array}\right.\right)=2\left(\mathrm{SO}^{2''}\left\{\begin{array}{l}\mathrm{O}\\\mathrm{O}\end{array}\right\}\mathrm{Ca}''\right)$$

Neutral phosphate of lime. Sulphuric acid. Sulphate of lime.



$$+\left(\begin{array}{l}\mathrm{PO}'''\left\{\begin{array}{l}\mathrm{OH}\\\mathrm{OH}\\\mathrm{O}\end{array}\right.\\\mathrm{PO}'''\left\{\begin{array}{l}\mathrm{O}\\\mathrm{OH}\\\mathrm{OH}\end{array}\right.\end{array}\left.\begin{array}{l}\\\\\mathrm{Ca}''\\\\\\\end{array}\right\}\right)$$

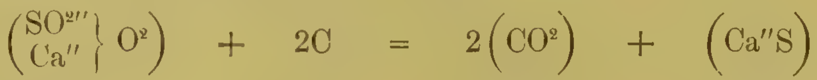
Biacid phosphate of lime.

This salt is generally designated as acid phosphate, and is used in the preparation of phosphorus.

**Sulphate of Calcium.**—Hydrated sulphate of calcium answering to the formula $\left(\left.\begin{array}{l}\mathrm{SO}^{2''}\\\mathrm{Ca}''\end{array}\right\}\mathrm{O}^2+2\,\mathrm{aq.}\right)$ is found in nature, and is known as gypsum; and also the anhydrous sulphate known in mineralogy under the name of the anhydrite. The latter is not used.

The hydrated sulphate is often found in transparent crystals, which are lance-shaped and cleave easily. It is very sparingly soluble in water, and its solubility does not vary with the temperature. Its density is 2·31.

When heated, gypsum loses its water of crystallization. If it has not been too strongly calcined, it may be again reformed by making it into a paste, which soon hardens. This constitutes plaster of Paris. When too strongly heated, it becomes, like the anhydrite, incapable of combining with water, and consequently no longer useful. When heated with reducing bodies such as carbon, the sulphate loses its oxygen and leaves a residue of sulphide of calcium.



$$\left(\left.\begin{array}{l}\mathrm{SO}^{2''}\\\mathrm{Ca}''\end{array}\right\}\mathrm{O}^2\right)+2\mathrm{C}=2\left(\mathrm{CO}^2\right)+\left(\mathrm{Ca}''\mathrm{S}\right)$$

Sulphate of lime. Carbon. Carbonic anhydride. Sulphide of calcium.

**Distinctive Characteristics of Calcic Salts.**—These salts may be recognized by the following characters:

1st. Alkaline carbonates precipitate them, and the precipitate, which is carbonate of calcium, is dissolved in a sufficient quantity of water by the assistance of a current of carbonic gas, but is again deposited on boiling.

2nd. Soluble sulphates and sulphuric acid precipitate them white, but as the sulphate of calcium dissolves in 500 parts of water, the precipitate is not obtained in very dilute solutions; in this case, however, the addition of alcohol to the liquid causes the precipitate to appear.

3rd. Oxalic acid and soluble oxalates produce a granular precipitate of oxalate of calcium which is insoluble in water, acetic acid, or the aqueous solution of hydrochlorate of ammonia, but soluble in diluted nitric and hydrochloric acids.

4th. Hydrofluosilicic acid does not disturb the solution of salts of lime.

5th. Chloride and nitrate of calcium are very soluble in alcohol.

## STRONTIUM $St''$.

Atomic weight of strontium = 87·5
Probable molecular weight = 87·5

## BARIUM $Ba''$.

Atomic weight of barium = 137.
Probable molecular weight = 137.

Barium and strontium are metals presenting such great analogies that we may consider them together.

These metals may be prepared by means of the galvanic battery, by a process similar to that described for the preparation of calcium. Barium has also been obtained by the action of sodium on the oxide of barium heated to redness.

Barium has a density of 4 or 5, and strontium 2·5. The first of these metals is silver white, and the second yellow in colour: neither have sufficient volatility to enable them to be distilled.

Barium and strontium act like calcium in their combinations. They are biatomic, and in consequence combine with one atom of oxygen or sulphur, or with two monatomic atoms. Thus we know:

The protoxide of barium or baryta ($Ba''O$), and the protoxide of strontium or strontia ($St''O$);

The monosulphides of barium and strontium ($Ba''S$) and ($St''S$);

The chlorides of barium and strontium ($Ba''Cl^2$) and ($St''Cl^2$), etc.

Besides an atom of one of these metals being capable of uniting with another biatomic atom, forming a group of the same atomicity as itself, we can also have oxides and sulphides of barium and strontium with several atoms of oxygen or sulphur, oxychlorides, etc. Of these compounds the only ones known are the binoxide of barium ($BaO^2$), which is obtained by heating the protoxide to dull redness in a current of air; the binoxide of strontium ($StO^2$), which is prepared by causing oxygenized water to act on the protoxide; and the oxychlorides ($BaOCl^2$) and ($StOCl^2$), which, according to the nomenclature already adopted by us for the analogous compounds of calcium, we will call chloride of barytyl and chloride of strontyl.

Finally, barium and strontium may combine with two atoms of hydroxyl, and give the hydrates

$$\left(Ba''\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right) \quad \text{and} \quad \left(St''\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)$$

These hydrates are formed by the direct action of water on the corresponding anhydrous oxides, but we cannot reform these anhydrous oxides by calcination. When submitted to the action of chlorine they lose water, and give the oxychlorides of which we have just spoken.

The principal minerals containing barium and strontium are their sulphates. All their other compounds may be prepared from these salts by the following process:

The sulphate is calcined with charcoal, which reduces it to the state of sulphide:

$$\underset{\text{Sulphate of barium.}}{(SBa''O^4)} + \underset{\text{Carbon.}}{2C} = \underset{\text{Carbonic anhydride.}}{2(CO^2)} + \underset{\text{Sulphide of barium.}}{(Ba''S)}$$

This sulphide is then treated with nitric acid, and a nitrate is produced. The nitrate, when calcined in a porcelain capsule, leaves anhydrous baryta or strontia (anhydrous oxide of barium or strontium). In presence of water baryta and strontia pass to the state of hydrates. These react with the various acids, forming all the known salts of the two metals.

The aqueous solutions of sulphide of barium or strontium may be precipitated by an alkaline carbonate. Thus an insoluble carbonate is formed, from which all the other salts may be prepared, simply by treating it with the different acids.

**Distinctive Characteristics of Salts of Barium and Strontium.**—The salts of barium and strontium may be recognized by the following characters:

1st. They are precipitated by carbonate of ammonium, which enables them to be distinguished from alkaline and magnesian salts, but not from salts of calcium.

2nd. Very dilute solutions of sulphuric acid or soluble sulphates, and even the solution of sulphate of calcium, precipitate these salts. This property distinguishes them from the salts of calcium, which are not disturbed by the solution of the latter of these reagents.

3rd. The salts of barium and strontium are distinguished from one another by their reactions with hydrofluosilicic acid and the dilute solution of chromate of potassium, which only precipitate the salts of barium. Chloride of strontium is soluble in absolute alcohol, in which the chloride of barium is quite insoluble.

## MAGNESIUM $Mg''$.

Atomic weight = 24. Probable molecular weight = 24.

Messrs. Deville and Caron have obtained magnesium by the following process:

A mixture is made of

| | |
|---|---|
| Anhydrous chloride of magnesium . . . . | 6 parts |
| Sodium in fragments . . . . . . . . . . | 1 ,, |
| Fluoride of calcium . . . . . . . . . . | 1 ,, |
| Chloride of potassium . . . . . . . . . | 1 ,, |

This mixture is thrown into a red-hot crucible, and instantly covered. When the fusion is complete the mass is stirred. After cooling, the crucible is broken, and globules of magnesium are found, which are agglomerated by a fresh fusion. The sodium displaces the magnesium in this process. The chloride of potassium produces a double chloride which can be more easily acted on than simple chloride of magnesium; the fluoride of calcium merely facilitates the melting.

The density of magnesium is 1·743. This metal melts at a moderate heat, and may be distilled like zinc. Its vapour burns in air with great brilliancy, which is increased when the combustion takes place in oxygen.

Pure magnesium presents the whiteness and lustre of silver; it is not acted on by dry air, but moist air tarnishes it immediately. It easily dissolves in dilute acids, disengaging hydrogen, and can even decompose water when cold, but this latter decomposition is very slow.

Magnesium burns in chlorine and in the vapours of bromine, iodine, and sulphur. It is biatomic, and gives compounds of the same nature as barium, strontium, and calcium.

| | |
|---|---|
| Chloride of magnesium . . . . . . . | $MgCl^2$ |
| Bromide of magnesium . . . . . . . | $MgBr^2$. |
| Iodide of magnesium . . . . . . . | $MgI^2$. |
| Fluoride of magnesium . . . . . . . | $MgFl^2$. |
| Anhydrous oxide of magnesium . . . . | $MgO$. |
| Binoxide of magnesium . . . . . . . | $MgO^2$. |
| Hydrate of magnesium . . . . . . . | $Mg''\left\{\begin{matrix}OH\\OH\end{matrix}\right.$ |

and different oxy-salts arising from the substitution of magnesium for the basic hydrogen of acids, are known.

The chloride, oxide, hydrate, and, among the oxygenated salts, the carbonate and sulphate, are the only important compounds of magnesium.

**Chloride of Magnesium** ($Mg''Cl^2$).—When the oxide or hydrate of magnesium is dissolved in hydrochloric acid, water and chloride of magnesium are formed:

$$\underset{\text{Oxide of magnesium.}}{(Mg''O)} + \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Chloride of magnesium.}}{\left(Mg''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)}$$

But when the solution is evaporated an inverse reaction is produced, the water and the chloride of magnesium mutually decompose, hydrochloric acid is disengaged, and a residue of magnesic oxide remains.

In order to obtain anhydrous chloride of magnesium, chloride of ammonium is added to the solution of this salt, and a double chloride of magnesium and ammonium, which can be evaporated without decomposing, is formed; when the evaporation is completed, the temperature is raised sufficiently to volatilize the chloride of ammonium, and at length beautiful white micaceous laminæ of chloride of magnesium remain.

The decomposition of chloride of magnesium under the influence of boiling water is the chief fact to be noticed in the history of this salt. If ever the sulphate of sodium contained in saline waters were extracted, it would no longer be necessary to prepare this body, hydrochloric acid would cease to be an accessory product, and would become much dearer. The decomposition of chloride of magnesium by boiling water could then be used for its preparation. The waters of salt marshes, in fact, contain considerable quantities of chloride of magnesium, and by their distillation hydrochloric acid can be cheaply obtained.

The presence of chloride of magnesium in almost all waters is the reason that distilled water has always a slight acid reaction, unless a little lime be added in the retort.

**Oxide of Magnesium** ($\mathrm{MgO}$).—Anhydrous oxide of magnesium is obtained by calcining the hydrate, the carbonate, or the nitrate of this metal. It is ordinarily prepared from the carbonate: when a denser product is desired to be obtained the nitrate is used.

The oxide prepared by means of the carbonate is very light; in pharmacy it is called calcined magnesia.

Oxide of magnesium is a white body, infusible at the highest known temperature, and soluble in the proportion of $\frac{1 \text{ to } 2}{100000}$; it easily dissolves in acids, forming well-characterized salts; it is a basic anhydride. Calcined magnesia is used in medicine to relieve acidity of the stomach, and as an antidote in poisoning by arsenic.

**Hydrate of Magnesium** $\left(\left.\begin{matrix}\mathrm{Mg}''\\\mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right)$.—This is generally prepared by precipitating a salt of magnesia by potash or soda,

$$\underset{\text{Sulphate of magnesium.}}{\left(\left.\begin{matrix}\mathrm{SO}^{2\prime\prime}\\\mathrm{Mg}''\end{matrix}\right\}\mathrm{O}^2\right)} + \underset{\text{Potash.}}{2\left(\left.\begin{matrix}\mathrm{K}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\text{Sulphate of potassium.}}{\left(\left.\begin{matrix}\mathrm{SO}^{2\prime\prime}\\\mathrm{K}^2\end{matrix}\right\}\mathrm{O}^2\right)} + \underset{\text{Hydrate of magnesium.}}{\left(\left.\begin{matrix}\mathrm{Mg}''\\\mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right)}$$

collecting and well washing the precipitate. Calcined magnesia may also be mixed with water, and, if the calcination has not been too strong, the oxide and water combine directly.

$$\underset{\text{Oxide of magnesium.}}{(\mathrm{Mg}''\mathrm{O})} + \underset{\text{Water.}}{\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\text{Hydrate of magnesium.}}{\left(\left.\begin{matrix}\mathrm{Mg}''\\\mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right)}$$

This hydrate is found native in crystals, but these crystals have not been produced artificially.

Hydrate of magnesium is a base which enters into double decomposition with acids and their anhydrides; when it is amorphous it directly attracts the carbonic anhydride of the air.

**Sulphate of Magnesium** $\left(\left.\begin{matrix}\mathrm{SO}^{2\prime\prime}\\\mathrm{Mg}''\end{matrix}\right\}\mathrm{O}^2 + 7\,\mathrm{aq}\right)$.—Sulphate of magnesium is generally prepared from dolomite, which is the double carbonate of calcium and magnesium; it abounds in nature, and is the principal source of magnesian compounds. The mineral is treated by sulphuric acid, carbonic anhydride is disengaged, and the sulphates of calcium and magnesium are formed. The latter of these sulphates being very soluble, while the first is scarcely so at all, they can be easily separated by crystallization.

Sulphate of magnesium can also be extracted from sea-water and from certain mineral waters; it is colourless, and has a bitter and very disagreeable taste. It dissolves in 3·05 parts of water at 14°, and 1·38 at 97°. If crystallized from its aqueous solution at the ordinary temperature it assumes the form of small elongated prisms which contain 7 molecules of water. It may also be obtained crystallized with 1, 2, 5, 6 . . . . 12 molecules of water by varying the conditions of the experiment. At 0°, for instance, it crystallizes with 12 of water.

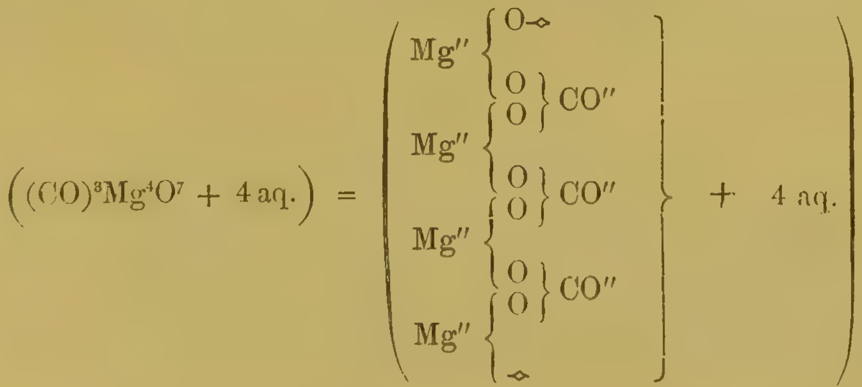
Sulphate of magnesium forms with alkaline sulphates double sulphates, which crystallize with six molecules of water. The double salt of magnesium and potassium answers to the formula :

$$\left( \left.\begin{matrix} SO^{2''} \\ Mg'' \end{matrix}\right\} O^2, \quad \left.\begin{matrix} SO^{2''} \\ K^2 \end{matrix}\right\} O^2 + 6\ aq. \right)$$

Sulphate of magnesium is used in medicine as a purgative : the dose is from half an ounce to an ounce.

It has been proved that sulphate of magnesium is formed when water saturated with sulphate of calcium is filtered through carbonate of magnesium; this fact explains the formation of the magnesian sulphates contained in mineral waters. In all probability, this salt is produced by the passage of water saturated by sulphate of calcium through dolomite earths.

**Carbonate of Magnesium.**—When the solution of sulphate of magnesium is precipitated by an alkaline carbonate, carbonic anhydride is disengaged and a precipitate is obtained, which, when washed, dried, and formed into cubes, is sold by chemists as white magnesia—*magnesia alba.* This body is a tetramagnesic tricarbonate answering to the formula :



$$\left((CO)^3Mg^4O^7 + 4\ aq.\right) = \left( \left.\begin{array}{lll} & O- & \\ Mg'' & & \\ & O & \\ & & CO'' \\ & O & \\ Mg'' & & \\ & O & \\ & & CO'' \\ & O & \\ Mg'' & & \\ & O & \\ & & CO'' \\ & O & \\ Mg'' & & \\ & - & \end{array}\right\} + 4\ aq. \right)$$

The following equation explains the formation of this compound:

$$\underset{\text{Sulphate of magnesium.}}{4\left(\left.\begin{matrix}SO^{2\prime\prime}\\Mg^{\prime\prime}\end{matrix}\right\}O^2\right)} + \underset{\text{Carbonate of potassium.}}{4\left(\left.\begin{matrix}CO^{\prime\prime}\\K^2\end{matrix}\right\}O^2\right)} + \underset{\text{Water.}}{4\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} =$$

$$\underset{\text{Sulphate of potassium.}}{4\left(\left.\begin{matrix}SO^{2\prime\prime}\\K^2\end{matrix}\right\}O^2\right)} + \underset{\text{Magnesia alba.}}{\left((CO^{\prime\prime})^3Mg^{\prime\prime 4}O^7 + 4\text{ aq.}\right)} + \underset{\text{Carbonic anhydride.}}{CO^2}$$

Magnesia alba has no taste, though it is slightly soluble; it dissolves in acids, giving salts of magnesium, carbonic anhydride being disengaged.

When white magnesia is suspended in water, and a current of carbonic anhydride gas is transmitted through the liquid, bicarbonate of magnesium, which dissolves, is formed. The solution of this salt, evaporated in a current of carbonic anhydride, leaves anhydrous neutral carbonate of magnesium $\left(\left.\begin{matrix}CO^{\prime\prime}\\Mg^{\prime\prime}\end{matrix}\right\}O^2\right)$; by spontaneous evaporation, the same solution deposits hydrated neutral carbonate; if the evaporation take place at the ordinary temperature, the crystals formed contain 3 aq.; they contain 5 aq. when the evaporation takes place at a low temperature: the latter crystals are efflorescent.

**Reactions of Salts of Magnesia.**—Soluble salts of magnesia are recognized by the following characteristics:

1st. They are not precipitated either by hydrosulphuric acid or by alkaline sulphides.

2nd. Carbonate of ammonium does not precipitate them.

3rd. Ammonia forms a precipitate of hydrate of magnesium, if the solution be neutral and do not contain ammoniacal salts; otherwise a double ammonio-magnesian salt, which is not decomposed by ammonia, would be formed. Even when the liquid is neutral, only half of the salt is decomposed, because an ammoniacal salt, which prevents the decomposition of the other half, is produced in the reaction.

4th. Phosphate of ammonium produces in solutions of magnesian salts a granulated crystalline precipitate of ammonio-magnesian phosphate.

## ZINC Zn.

Atomic weight = 32·75. Molecular weight = 32·75.

Zinc is extracted from blende (sulphide of zinc), and from calamine (carbonate of zinc). These ores are roasted; the blende is transformed into oxide by oxidation, while the carbonate also furnishes oxide, losing carbonic anhydride. The oxide produced, when calcined with charcoal, gives metallic zinc. The apparatus used for this reduction ought to be such that the metal melts and runs off as it becomes liberated;

then the method *per descensum* is said to be employed: but an apparatus may also be used in which zinc is reduced into vapour, and distilled; and this constitutes the method *per ascensum.*

The zinc of commerce is impure; it may be distilled, but it cannot be thereby freed from foreign metals. The best means of obtaining it in a state of purity consists in reducing pure oxide of zinc by carbon equally pure, obtained by calcining sugar.

Zinc is of a bluish-grey colour, and appears to be dimorphous; it fuses at 500°, and distils at red heat. It is very slightly flexible, but very malleable; when alloyed with other metals it becomes brittle, and acquires the same property when heated to 200°. Zinc has a density varying from 6·86 to 7·21, according as it is simply melted or laminated.

At the ordinary temperature zinc oxidizes on the surface, but the oxide formed preserves the metal from further oxidation; it burns brilliantly at red heat, emitting white fumes of oxide of zinc. It is thus that this oxide is manufactured.

Zinc decomposes the vapour of water at 100°; at the ordinary temperature it is substituted for the hydrogen of acids. We have seen that the preparation of hydrogen is founded on this property.

Silver, gold, platinum, bismuth, antimony, tin, cadmium, mercury, lead, etc., are displaced from their solutions by zinc.

When hot, the hydrates of potassium and sodium, and even the solution of ammonia, dissolve this metal with disengagement of hydrogen. In this case, with the fixed alkalies, alkaline zincates are formed.

$$\underset{\text{Potash.}}{2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} + \underset{\text{Zinc.}}{Zn''} = \underset{\text{Zincate of potassium.}}{\left(\left.\begin{matrix}Zn''\\K^2\end{matrix}\right\}O^2\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}}$$

Being biatomic, zinc combines with two atoms of chlorine, bromine, or iodine, giving a chloride $\left(Zn''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)$, a bromide $\left(Zn''\left\{\begin{matrix}Br\\Br\end{matrix}\right.\right)$, or an iodide $\left(Zn''\left\{\begin{matrix}I\\I\end{matrix}\right.\right)$. With oxygen it forms a protoxide ($Zn''O$) and a binoxide ($Zn''O^2$). The protoxide corresponds to the hydrate $\left(\left.\begin{matrix}Zn''\\H^2\end{matrix}\right\}O^2\right)$, which furnishes a series of salts by the substitution of acid radicles for the typical hydrogen it contains. Finally, zinc forms with sulphur a monosulphide ($Zn''S$).

### Combinations of Zinc with Monatomic Metalloids.

**Chloride of Zinc** $\left(Zn''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)$.—This body is formed when zinc is heated in a current of chlorine: in this case the metal burns and is converted into chloride; but it is obtained more rapidly and cheaply by dissolving zinc in hydrochloric acid.

$$\underset{\text{Zinc.}}{Zn''} \quad + \quad \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} \quad = \quad \underset{\text{Chloride of zinc.}}{\left(Zn''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)} \quad + \quad \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}}$$

When the metal is dissolved, the liquid is filtered in order to separate some impurities which are contained in the zinc of commerce, and which do not dissolve; then it is evaporated to dryness, and when this is completed the residue is melted by heat, and it is then poured on to a clean marble slab; as soon as it is solidified, it is pounded, and placed in a bottle accurately stoppered. If it were allowed to cool in the air its surface would absorb moisture. Chemists formerly called this substance butter of zinc.

If instead of evaporating to dryness, the process be arrested when the liquor has become highly concentrated, the chloride of zinc is deposited on cooling, in hydrated crystals.

Chloride of zinc is of a greyish colour and melts at 250°; it begins to emit vapours at 400°, and is very deliquescent; it produces great heat on dissolving in water, and has such affinity for this liquid that it destroys living tissues, seizing the water they contain. Surgeons thus use it as a caustic.

Alcohol dissolves chloride of zinc. If such a solution be heated, the alcohol is dehydrated; and, according to the proportion of chloride of zinc that has been employed, ethylene ($C^2H^4$) or ether ($C^4H^{10}O$) is produced.

$$\underset{\text{Alcohol.}}{(C^2H^6O)} \quad = \quad \underset{\text{Water.}}{(H^2O)} \quad + \quad \underset{\text{Ethylene.}}{(C^2H^4)}$$

$$\underset{\text{Alcohol.}}{2\,(C^2H^6O)} \quad = \quad \underset{\text{Water.}}{(H^2O)} \quad + \quad \underset{\text{Ether.}}{(C^4H^{10}O)}$$

**Bromide of Zinc** $\left(Zn''\left\{\begin{matrix}Br\\Br\end{matrix}\right.\right)$ is prepared like the chloride, and possesses analogous properties.

**Iodide of Zinc** $\left(Zn''\left\{\begin{matrix}I\\I\end{matrix}\right.\right)$.—This is prepared by pounding iodine and zinc filings under water. It is a white substance, soluble in water, crystallizes in needles, and has a styptic, disagreeable taste. This compound could be used in medicine, according to Bouchardat, in preference to iodide of lead.

### COMBINATIONS OF ZINC WITH BIATOMIC METALLOIDS.

**Protoxide of Zinc** ($Zn''O$).—In the arts oxide of zinc is prepared directly by the combustion of the metal. For this purpose the zinc is heated until it emits vapours, which are lighted, the fumes are then carried by a current of air into a series of chambers, where the oxide of zinc is deposited.

The oxide of zinc thus prepared was formerly called *lana philosophica*, *nihilum album*, *flowers of zinc*, and *pomphalis*.

Oxide of zinc may also be prepared by heating the hydrate of the metal, or by calcining the nitrate or carbonate, or by heating the bisulphite of zinc, which is itself obtained by the action of sulphurous anhydride on blende (sulphide of zinc) pulverized and suspended in water.

Oxide of zinc is white at the ordinary temperature: it becomes yellow when heated, and regains its original colour on cooling. When procured by the calcination of the metal, it is light and flocculent; when prepared by means of the bisulphite, it appears spongy and is also very light; when obtained by calcining the nitrate, it is pulverulent and heavy.

Oxide of zinc is fixed; water only dissolves $\frac{1}{100000}$, but yet the solution changes the colour of litmus.

Oxide of zinc is a basic anhydride which enters into double decomposition with acids, and gives well-defined salts which are isomorphous with those of magnesium.

It is employed in medicine as an antispasmodic, and has been recommended for epilepsy. It is now used in painting, as a substitute for white lead (carbonate of lead).

**Hydrate of Zinc** $\left(\left.\begin{matrix}Zn''\\H^2\end{matrix}\right\}O^2\right)$.—When an alkaline solution is added to the solution of a salt of zinc, a precipitate is formed which, collected on a filter and well washed, constitutes the hydrate of zinc.

This hydrate loses a molecule of water under the influence of heat, and leaves a residue of anhydrous oxide of zinc.

Hydrate of zinc enters into double decomposition with acids, and gives salts arising from the substitution of the radicles of these acids for its typical hydrogen. It is a powerful base, but in presence of energetic bases it can also exchange its hydrogen for a metal and furnish zincates; in this case it acts as a weak acid.

$$\text{1st.}\ \underset{\substack{\text{Hydrate of}\\\text{zinc.}}}{\left(\left.\begin{matrix}Zn''\\H^2\end{matrix}\right\}O^2\right)} + 2\underset{\text{Nitric acid.}}{\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)} = \underset{\text{Nitrate of zinc.}}{\left(\left.\begin{matrix}Zn''\\(NO^2)^2\end{matrix}\right\}O^2\right)} + 2\underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

$$\text{2nd.}\ \underset{\substack{\text{Hydrate of}\\\text{zinc.}}}{\left(\left.\begin{matrix}Zn''\\H^2\end{matrix}\right\}O^2\right)} + 2\underset{\substack{\text{Hydrate of}\\\text{potassium.}}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = 2\underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\substack{\text{Zincate of}\\\text{potassium.}}}{\left(\left.\begin{matrix}Zn''\\K^2\end{matrix}\right\}O^2\right)}$$

**Sulphate of Zinc** $\left(\left.\begin{matrix}SO^{2''}\\Zn''\end{matrix}\right\}O^2\right)$.—In the laboratory, sulphate of zinc is prepared by dissolving metallic zinc in dilute sulphuric acid:

$$\underset{\text{Zinc.}}{Zn''} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)} = \underset{\substack{\text{Sulphate of}\\\text{zinc.}}}{\left(\left.\begin{matrix}SO^2\\Zn''\end{matrix}\right\}O^2\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}}$$

For this purpose the residue of the preparation of hydrogen is utilised: this solution has only to be filtered and crystallized. In the arts, native blende (sulphide of zinc) is roasted; it absorbs oxygen from the air and thus passes to the state of sulphate. The sulphate is then dissolved in water, the solution decanted, and crystallized.

$$\underset{\text{Sulphide of zinc.}}{(\mathrm{Zn}''\mathrm{S})} + \underset{\text{Oxygen.}}{2\left(\left.\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\}\right)} = \underset{\text{Sulphate of zinc.}}{\left(\left.\begin{matrix}\mathrm{SO}^{2''}\\ \mathrm{Zn}''\end{matrix}\right\}\mathrm{O}^2\right)}$$

For convenience of carriage it is melted in its water of crystallization and poured into lumps.

Sulphate of zinc dissolves in two or three times its weight of water at the ordinary temperature; at the same temperature it crystallizes with 7 molecules of water of crystallization; it can also crystallize with different quantities of water when the conditions under which the crystallization takes place are varied. In all cases the crystals of sulphate of zinc are isomorphous with those of sulphate of magnesium, which contain the same quantity of water.

Sulphate of zinc combines with alkaline sulphate to give double salts, which crystallize with 6 molecules of water. The double salt of zinc and potassium answers to the formula

$$\left(\left.\begin{matrix}\mathrm{SO}^{2''}\\ \mathrm{Zn}''\end{matrix}\right\}\mathrm{O}^2,\quad \left.\begin{matrix}\mathrm{SO}^{2''}\\ \mathrm{K}^2\end{matrix}\right\}\mathrm{O}^2 + 6\ \mathrm{aq.}\right)$$

When strongly heated, sulphate of zinc is decomposed and leaves a residue of oxide of zinc.

**Binoxide of Zinc** $(\mathrm{Zn}''\mathrm{O}^2)$.—This substance is obtained by treating the protoxide with oxygenated water.

$$\underset{\text{Protoxide of zinc.}}{(\mathrm{Zn}''\mathrm{O})} + \underset{\text{Oxygenated water.}}{(\mathrm{H}^2\mathrm{O}^2)} = \underset{\text{Water.}}{(\mathrm{H}^2\mathrm{O})} + \underset{\text{Binoxide of zinc.}}{(\mathrm{Zn}''\mathrm{O}^2)}$$

It is a body of slight stability.

**Sulphide of Zinc** $(\mathrm{Zn}''\mathrm{S})$.—This body exists in nature crystallized in regular octahedra, and has received the name of blende. It may be obtained artificially by precipitating a salt of zinc by a soluble sulphide.

$$\underset{\text{Sulphate of zinc.}}{\left(\left.\begin{matrix}\mathrm{SO}^{2''}\\ \mathrm{Zn}''\end{matrix}\right\}\mathrm{O}^2\right)} + \underset{\text{Sulphide of potassium.}}{\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{K}\end{matrix}\right\}\mathrm{S}\right)} = \underset{\text{Sulphate of potassium.}}{\left(\left.\begin{matrix}\mathrm{SO}^{2''}\\ \mathrm{K}^2\end{matrix}\right\}\mathrm{O}^2\right)} + \underset{\text{Sulphide of zinc.}}{\left(\mathrm{Zn}''\mathrm{S}\right)}$$

When roasted, sulphide of zinc is converted either into sulphate or into sulphurous anhydride and oxide, according to the temperature.

$$\text{1st. } \underset{\text{Sulphide of zinc.}}{\left(\mathrm{Zn}''\mathrm{S}\right)} + \underset{\text{Oxygen.}}{2\left(\left.\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\}\right)} = \underset{\text{Sulphate of zinc.}}{\left(\left.\begin{matrix}\mathrm{SO}^{2''}\\ \mathrm{Zn}''\end{matrix}\right\}\mathrm{O}^2\right)}$$

$$\text{2nd. } \underset{\text{Sulphide of zinc.}}{2\left(\mathrm{Zn}''\mathrm{S}\right)} + \underset{\text{Oxygen.}}{3\left(\left.\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\}\right)} = \underset{\text{Sulphurous anhydride.}}{2\left(\mathrm{SO}^2\right)} + \underset{\text{Oxide of zinc.}}{2\left(\mathrm{Zn}''\mathrm{O}\right)}$$

Sulphide of zinc dissolves in acids, disengaging hydrosulphuric acid.

$$\underset{\text{Sulphide of zinc.}}{\left(\text{Zn}''\text{S}\right)} + \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}\text{H}\\ \text{Cl}\end{matrix}\right\}\right)} = \underset{\text{Chloride of zinc.}}{\left(\text{Zn}''\left\{\begin{matrix}\text{Cl}\\ \text{Cl}\end{matrix}\right.\right)} + \underset{\text{Sulphuretted hydrogen.}}{\left(\left.\begin{matrix}\text{H}\\ \text{H}\end{matrix}\right\}\text{S}\right)}$$

**Carbonate of Zinc.**—Carbonate of zinc is found native, and the mineral has received the name of calamine. It is only employed in the metallurgy of zinc.

**Reactions of Salts of Zinc.**—Salts of zinc are recognized by the following characters:

1st. Hydrosulphuric acid does not precipitate them from solution, unless the salt be derived from a weak acid like acetic acid, in which case a white precipitate of sulphide of zinc is formed.

2nd. Sulphide of ammonium forms a white precipitate of sulphide of zinc, which is soluble in dilute hydrochloric acid.

3rd. Potash produces a white precipitate of hydrate of zinc, which is soluble in an excess of the reagent.

4th. Ammonia acts like potash.

5th. Carbonates of potassium and sodium with salts of zinc give a white precipitate of carbonate of zinc, which is insoluble in an excess of the reagent.

6th. Carbonate of ammonium acts in the same manner, with the slight difference that the precipitate dissolves in an excess of the reagent.

## CADMIUM Cd.

Atomic weight = 112. Molecular weight = 112.

Cadmium is almost always contained in the ores of zinc. When these ores are submitted to metallurgic operations, the cadmium distils first, being the more volatile; it may be obtained pure by successive distillations.

Cadmium is white, very ductile, and very malleable; its density is 8·7; it melts below red heat and its vapour burns brilliantly in air.

It forms compounds entirely analogous to those of zinc. Thus we know:

| | |
|---|---|
| An oxide . . . . . . . . . . | $CdO$ |
| A sulphide . . . . . . . . . | $CdS$ |
| A hydrate . . . . . . . . . | $Cd''\left\{\begin{matrix}OH\\ OH\end{matrix}\right.$ |
| A chloride . . . . . . . . . | $CdCl^2$ |
| A bromide . . . . . . . . . | $CdBr^2$ |
| An iodide . . . . . . . . . | $CdI^2$, etc. |

The oxide and the hydrate of cadmium enter into double decomposition with acids, giving rise to salts that are isomorphous with those of zinc and magnesium.

These salts possess the following properties:

1st. Hydrosulphuric acid added to their solutions gives rise to a yellow precipitate that is insoluble in alkaline sulphides but dissolves in hydrochloric acid. This precipitate forms even when the salt of cadmium is mixed with a solution of cyanide of potassium.

2nd. Potash and soda form a white precipitate of hydrate of cadmium, which is insoluble in an excess of the reagent.

3rd. Ammonia gives the same precipitate, but an excess of the reagent dissolves it.

## COPPER Cu.

Atomic weight = 63. Probable molecular weight = 63.

Copper is found native, but the principal ore of this metal is a double sulphide of copper and iron. This ore is first roasted, which process transforms the sulphide of iron into oxide of iron and sulphurous anhydride. The oxide of iron passes into the siliceous scoriæ in the state of fusible silicate. The product of this first operation is called matt, and when this is treated in precisely the same manner as just described it is entirely deprived of iron, and gives what is called white matt.

When, again, this white matt is roasted impure copper is obtained; the sulphide of copper is really transformed into sulphurous anhydride and oxide of copper, and this latter reacts on the undecomposed sulphide, forming copper and sulphurous anhydride.

$$\underset{\text{Subsulphide of copper.}}{(Cu^2S)} + \underset{\text{Protoxide of copper.}}{2(CuO)} = \underset{\text{Copper.}}{4Cu} + \underset{\text{Sulphurous anhydride.}}{SO^2}$$

On roasting the impure copper in a silex kiln, the formation of a certain quantity of oxide takes place, which entirely eliminates the sulphur, at the same time the oxides of the foreign metals unite with the silex of the kiln and form silicates which pass into the scoriæ.

Finally, to prevent it containing oxide it is melted, charcoal is placed on its surface, and the mass is stirred with green wood. The carbon gases, which are disengaged under the influence of heat, complete the reduction of the oxide of copper which is disseminated in the metallic mass.

These two last operations are called refining.

Chemically pure copper may be obtained by reducing the oxide of this metal by hydrogen.

For this process, pure oxide of copper is placed in a small globe blown in the middle of a glass tube (fig. 34); one of the ends of this tube communicates with an apparatus in which hydrogen is produced; care must be taken, however, to interpose a drying tube between the globe and this apparatus, and the tube is allowed to communicate freely with the atmosphere by its other extremity.

When the hydrogen has passed for a sufficient length of time for the whole of the air to be expelled, the oxide of copper is heated by a spirit lamp*, water is formed, and the copper becomes free.

$$\underset{\text{Oxide of copper.}}{(Cu''O)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Copper.}}{Cu''}$$

The operation is complete when vapour of water no longer passes off.

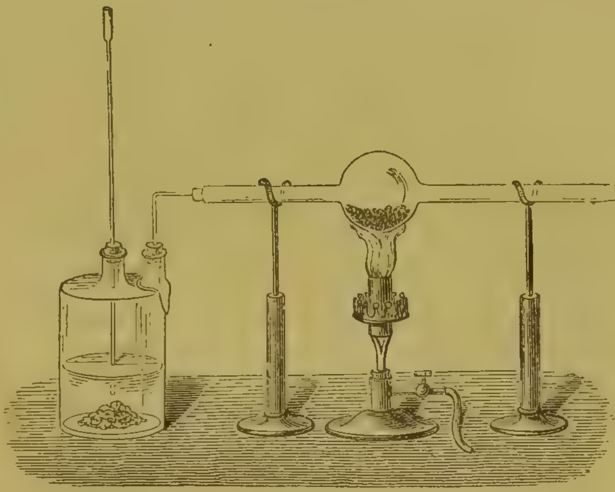


Fig. 34.

LEEDS SCHOOL OF MEDICINE

Copper is red, and has sufficient malleability to enable it to be reduced into transparent leaves; it is very ductile and very tenacious. Its density is 8·85.

It is obtained artificially, crystallized in cubes, which form it also assumes in nature.

Copper when rubbed acquires a disagreeable odour. It melts at about 778°, and does not oxidize in dry air at the ordinary temperature; when heated, it oxidizes without incandescence, and, exposed to moist air, it becomes covered with a coating of hydrated carbonate of copper (verdigris), but this coating preserves the metal from further alteration.

Nitric acid acts on copper when cold, and sulphuric acid dissolves it when hot; in the first case, binoxide of nitrogen and nitrate of copper are produced; and sulphate of copper and sulphurous anhydride are formed in the second.

1st.

$$\underset{\text{Nitric acid.}}{8\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)} + \underset{\text{Copper.}}{3Cu''} = \underset{\text{Nitrate of copper.}}{3\left[\left.\begin{matrix}(NO^2)^2\\Cu''\end{matrix}\right\}O^2\right]}$$

$$+ \underset{\text{Water.}}{4\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Binoxide of nitrogen.}}{2\,(NO)}$$

---

* If heat were applied before the air had been expelled, an explosion would take place, owing to the explosive mixture which would form in the globe.

$$\text{2nd. } \underset{\text{Sulphuric acid.}}{2\left(\left.\begin{matrix}SO^{2\prime\prime}\\ H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Copper.}}{Cu''} = \underset{\text{Sulphate of copper.}}{\left(\left.\begin{matrix}SO^{2\prime\prime}\\ Cu''\end{matrix}\right\}O^2\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)} + \underset{\text{Sulphurous anhydride.}}{(SO^2)}$$

In presence of acids copper readily absorbs oxygen from the air; it also oxidizes in presence of ammonia and dissolves, forming a beautiful blue liquid.

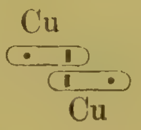
Copper when previously heated burns in chlorine, forming bichloride of copper. It combines directly with sulphur, phosphorus, arsenic, bromine, and most metals.

Copper forms two series of compounds. Being biatomic, it can combine directly with two monatomic radicles, or with one biatomic radicle like itself, and thus be saturated. Thence a whole series of compounds, known as per-compounds or cupric compounds. These are:

| | |
|---|---|
| The bichloride of copper | $Cu''Cl^2$ |
| The bibromide ,, | $Cu''Br^2$ |
| The bifluoride ,, | $Cu''Fl^2$ |
| Perhydrate of copper | $Cu''(OH)^2$ |
| The protoxide of copper | $Cu''O$ |
| The protosulphide of copper | $Cu''S$ |

and the different oxygenated per-salts resulting from the substitution of the radicles of acids for the hydrogen of the perhydrate.

On account of the biatomicity of copper, it may also happen that two atoms of this metal unite, only exchanging with one another a single atomicity and forming the biatomic group $Cu^2$, as the following figure shows:



$= (Cu^2)''$

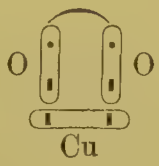
The group $Cu^2$ being biatomic, can also be combined, quite as well as the atom Cu, with chlorine, bromine, iodine, etc., and as the combinations it forms are of sufficient stability, we have a second series of copper compounds, known as sub- or cuprous compounds, in which, instead of the simple atom $Cu''$, the group $Cu^2$ acts. These are:

| | |
|---|---|
| The protochloride | $Cu^2Cl^2$ |
| The protobromide | $Cu^2Br^2$ |
| The prot-iodide | $Cu^2I^2$ |
| The protofluoride | $Cu^2Fl^2$ |
| The sub-oxide | $Cu^2O$ |
| The sub-sulphide | $Cu^2S$ |

and very instable protosalts, resulting from the substitution of the biatomic group $Cu^2$ for an equal number of atoms of the typical hydrogen of acids.

Besides these two series of compounds, copper also forms with oxygen a binoxide ($CuO^2$) and a cupric acid, the composition of which has not yet been exactly determined.

The biatomicity of oxygen explains how several atoms of this body may unite with a single atom of copper: two atoms of oxygen can each exchange one atomicity with copper and one with each other, as we see by the following figure:



## Cupric Compounds.

Those of these compounds requiring notice are: the bichloride, the protosulphide, the protoxide, the hydrate, the sulphate, the nitrate and the carbonates.

**Bichloride of Copper** $\left(Cu''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)$.—This compound is formed by the direct action of chlorine on copper; it is also formed when the protoxide is dissolved in hydrochloric acid.

$$\underset{\text{Copper.}}{Cu''} + \underset{\text{Chlorine.}}{\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}} = \underset{\text{Perchloride of copper.}}{\left(Cu''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)}$$

$$\underset{\text{Protoxide of copper.}}{\left(Cu''O\right)} + \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Bichloride of copper.}}{\left(Cu''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)}$$

Bichloride of copper is soluble in water and in alcohol; its aqueous solution, concentrated by heat, on cooling deposits hydrated crystals which have for formula ($Cu''Cl^2 + 2\,aq.$) These crystals have the form of elongated needles of a greenish-blue colour.

The alcoholic solution of this salt burns with a magnificent green flame.

**Protosulphide of Copper** ($Cu''S$).—This body does not exist in nature in an isolated state; it is obtained by transmitting a current of sulphuretted hydrogen through an aqueous solution of a cupric salt, the bichloride, for instance:

$$\underset{\text{Bichloride of copper.}}{\left(Cu''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)} + \underset{\text{Hydrosulphuric acid.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}S\right)} = \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Sulphide of copper.}}{\left(Cu''S\right)}$$

It is precipitated in the form of a black mass easily affected by air, whose oxygen it attracts, and is converted into sulphate.

$$\underset{\text{Protosulphide of copper.}}{\left(Cu''S\right)} + \underset{\text{Oxygen.}}{2\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\right)} = \underset{\text{Sulphate of copper.}}{\left(\left.\begin{matrix}SO^{2''}\\Cu''\end{matrix}\right\}O^2\right)}$$

Protosulphide of copper loses half its sulphur when heated, and is transformed into sub-sulphide.

$$\underset{\text{Protosulphide of copper.}}{4(CuS)} = \underset{\text{Subsulphide of copper.}}{2(Cu^2S)} + \underset{\text{Sulphur.}}{\left.\begin{matrix}S\\S\end{matrix}\right\}}$$

**Protoxide of Copper** ($CuO$).—This oxide may be obtained, 1st, by heating copper in air: a layer of oxide, which is easily removed, forms on the surface of the metal; 2ndly, by calcining the nitrate of copper; and, 3rdly, by heating cupric hydrate: if this latter body be boiled with water, it will become dehydrated.

Whatever process be employed in its preparation, and whatever slight differences there may be in the physical properties of the oxide, which may be more or less compact, this compound always possesses the following properties:

It is a black amorphous powder, which resists a very high temperature without decomposing, and without melting. But when too strongly heated all the mass is united into a single lump of very great hardness, which, when pounded, has a yellowish colour. This oxide appears to be in a particular allotropic state. M. Lieben has observed that it can then be aggregated at a lower temperature than when it has not been overheated. It, however, loses this property if it be heated many times at a temperature which is insufficient to aggregate it, and if it be then allowed to cool.

Protoxide of copper is a basic anhydride, which enters into double decomposition with acids, giving per-salts. It is much used in laboratories in making organic analyses.

**Hydrate of Copper** $\left(\left.\begin{matrix}Cu''\\H^2\end{matrix}\right\}O^2\right)$.—This hydrate is obtained by precipitating the solution of the bichloride or sulphate, or any other per-salt of copper, by an alkaline base. The precipitate which forms should be well washed, and dried at the ordinary temperature; its colour is dirty blue.

The hydrate of copper is dehydrated by heat; and, if the liquor from which it is precipitated be boiled, it loses water, and is transformed into anhydrous oxide:

$$\underset{\text{Copper.}}{\left(\left.\begin{matrix}Cu''\\H^2\end{matrix}\right\}O^2\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Protoxide of copper.}}{\left(Cu''O\right)}$$

Hydrate of copper dissolves in ammonia, forming a beautiful blue solution.

**Persulphate of Copper** $\left(\left.\begin{matrix}SO^{2''}\\Cu''\end{matrix}\right\}O^2\right)$.—This substance is prepared in the laboratory by acting on hot copper by concentrated sulphuric acid, dissolving in water, and crystallizing.

$$\underset{\text{Copper.}}{\mathrm{Cu}''} + \underset{\text{Sulphuric acid.}}{2\left(\left.\begin{matrix}\mathrm{SO}^{2\prime\prime}\\ \mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right)} = \underset{\text{Sulphate of copper.}}{\left(\left.\begin{matrix}\mathrm{SO}^{2\prime\prime}\\ \mathrm{Cu}''\end{matrix}\right\}\mathrm{O}^2\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Sulphurous anhydride.}}{\left(\mathrm{SO}^2\right)}$$

The residue of the preparation of sulphurous anhydride is thus utilized. In the arts, sulphide of copper is heated in air. This body absorbs oxygen from the air, and is transformed into sulphate, which is separated from the undecomposed ore by lixiviation and evaporation.

The sulphate of copper of commerce almost always contains sulphate of iron: the best method of obtaining the salt free from iron consists in dissolving it in water, and precipitating it by sulphuretted hydrogen from the solution previously acidulated. The copper is precipitated alone: this precipitate, well washed, and exposed to contact with air and water, is transformed into a sulphate, which is crystallized after the solution has been filtered. Sulphate of copper is known in commerce as blue vitriol or blue copperas. It is insoluble in alcohol, but soluble in water; it crystallizes from its solution in the latter liquid in blue oblique parallelopipeds. These crystals are hydrated, and have for formula $\left(\left.\begin{matrix}\mathrm{SO}^{2\prime\prime}\\ \mathrm{Cu}''\end{matrix}\right\}\mathrm{O}^2 + 5\ \mathrm{aq.}\right)$

When hydrated sulphate of copper is heated to 100°, it loses 4 aq., and at 243° it loses the remainder, and becomes anhydrous. It then forms a white powder, which resembles flour. The smallest quantity of water restoring it to its blue colour, this body becomes a valuable test for the presence of water.

The crystals of sulphate of copper are isomorphous with those of the sulphates of magnesium, zinc, and cadmium, when these contain, like it, five molecules of water. This salt forms double sulphates with alkaline sulphates. It combines with the sulphates of magnesium, zinc, the sub-sulphate of iron, etc., giving crystals which contain five molecules of water when the copper predominates, and seven when it is the other metal which does so: these crystals are always isomorphous among themselves when they contain the same quantity of water.

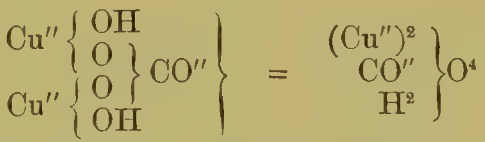
When strongly heated, the sulphate of copper is decomposed into oxygen, sulphurous anhydride, and protoxide of copper.

If this salt be precipitated by an insufficient quantity of base, an insoluble basic sulphate is produced, which is green.

When a quantity of ammonia sufficient to dissolve the precipitate formed is added to a solution of sulphate of copper, and alcohol is afterwards poured into the blue liquor produced, a beautiful blue precipitate is obtained, which has received the name of ammoniacal sulphate of copper, and whose composition is $\left(\left.\begin{matrix}\mathrm{SO}^{2\prime\prime}\\ \mathrm{Cu}''\end{matrix}\right\}\mathrm{O}^2,6\mathrm{NH}^3+\mathrm{H}^2\mathrm{O}\right)$.

**Nitrate of Copper** $\left(\mathrm{Cu}''\left\{\begin{matrix}\mathrm{ONO}^2\\ \mathrm{ONO}^2\end{matrix}\right.\right)$.—Nitrate of copper is prepared by dissolving the metal in nitric acid, evaporating the liquid, and allowing it to cool. The salt is deposited in large blue hydrated crystals, which, when heated, first melt in their water of crystallization, then this water is vaporized, and the anhydrous nitrate is decomposed; a green basic nitrate first forms, the decomposition then becomes still more complete, and, finally, there remains a residue of oxide of copper.

**Carbonates of Copper.**—The carbonate obtained by pouring carbonate of sodium into a solution of sulphate of copper is a dicupric carbonate, and is bibasic. Its formula is:



$$\left.\begin{array}{l}\mathrm{Cu''}\left\{\begin{array}{l}\mathrm{OH}\\ \mathrm{O}\end{array}\right.\\ \qquad\qquad\left.\begin{array}{l}\\ \end{array}\right\}\mathrm{CO''}\\ \mathrm{Cu''}\left\{\begin{array}{l}\mathrm{O}\\ \mathrm{OH}\end{array}\right.\end{array}\right| = \left.\begin{array}{c}(\mathrm{Cu''})^2\\ \mathrm{CO''}\\ \mathrm{H}^2\end{array}\right\}\mathrm{O}^4$$

This body has the same composition as the natural carbonate known as *malachite.* Malachite is of a beautiful green colour, and is used in compact blocks for ornamental purposes. Where it abounds, as in Siberia, for instance, malachite is used as a copper ore. It is a very rich one.

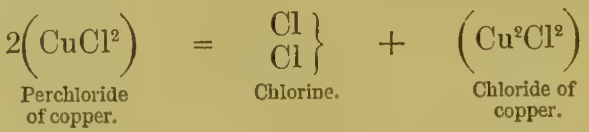
There also exists native a hydrated tricupric carbonate of a beautiful blue colour, known as *chessylite.*

Finally, the verdigris which forms on the surface of copper is also a hydrated carbonate of copper, but it must not be confounded with the verdigris of commerce, which is the sub-acetate of copper.

## CUPROUS COMPOUNDS.

**Protochloride of Copper** ($Cu^2Cl^2$).—The most simple method of preparing this body consists in dissolving metallic copper in aqua-regia containing an extremely small quantity of nitric acid, and adding water to the solution; the protochloride of copper precipitates in the form of a white crystalline powder. This compound may also be prepared by dissolving the sub-oxide of copper in boiling hydrochloric acid, and leaving the liquid to cool, from which small colourless tetrahedra of protochloride of copper are deposited.

It may also be obtained by heating perchloride of copper, which loses half of its chlorine.



$$\underset{\text{Perchloride of copper.}}{2\left(\mathrm{CuCl}^2\right)} = \underset{\text{Chlorine.}}{\left.\begin{array}{c}\mathrm{Cl}\\ \mathrm{Cl}\end{array}\right\}} + \underset{\text{Chloride of copper.}}{\left(\mathrm{Cu}^2\mathrm{Cl}^2\right)}$$

Chloride of copper is a white substance, sparingly soluble in water, but soluble in hydrochloric acid and in ammonia; it becomes green in the air, absorbing oxygen and becoming transformed into oxychloride ($Cu^2Cl^2O$). It also absorbs carbonic oxide, but disengages the gas when its solution is boiled. Cuprous chloride dissolved in ammonia, gives, with gaseous carbides of hydrogen of the series $C^nH^{2n-2}$, explosive precipitates, which, when heated with hydrochloric acid, disengage the hydrocarbide whose elements they contain. This property is utilized in organic chemistry.

**Sub-sulphide of Copper** ($Cu^2S$).—Subsulphide of copper is found native in beautiful crystals belonging to the cubic system. They are black, and have a slight metallic lustre; they are soft enough to be cut with a knife, and melt in the flame of a taper. Their density is 5·0.

This substance is prepared artificially by calcining copper with an excess of sulphur, which excess evaporates during the calcination. That no copper may be left unacted on, the product of this first operation is pounded and again calcined with sulphur.

When heated in air, it gives sulphate of copper if the temperature be not too elevated; otherwise, it is transformed into oxide of copper and sulphurous anhydride, absorbing oxygen. When the sulphide is heated with oxide of copper, a disengagement of sulphurous anhydride takes place, and a residue of metallic copper is left.

$$\underset{\substack{\text{Sub-sulphide}\\ \text{of copper.}}}{(Cu^2S)} + \underset{\substack{\text{Protoxide}\\ \text{of copper.}}}{2\,(CuO)} = \underset{\text{Copper.}}{4Cu} + \underset{\substack{\text{Sulphurous}\\ \text{anhydride.}}}{(SO^2)}$$

**Sub-oxide of Copper** ($Cu^2O$).—This substance is found native. It is sometimes found in compact masses and sometimes in regular octahedral crystals of a red colour; it may be obtained artificially in the form of a red powder in various ways.

If acetate of copper be boiled with glucose, a red crystalline powder, the sub-oxide of copper, is precipitated.

In the arts this body is usually prepared by calcining a mixture of

| | |
|---|---|
| Sulphate of copper . . . . | 100 parts |
| Dry carbonate of sodium . . | 28 ,, |
| Copper filings . . . . . . | 25 ,, |

The product of this operation must undergo frequent washings.

Sub-oxide of copper melts without altering when heated protected from the air; it is transformed into protoxide when heated in air.

Hydrochloric acid enters into double decomposition with it, and converts it into protochloride; this oxide is therefore a basic anhydride.

Nitric acid yields oxygen to it, and causes it to pass to the state of pernitrate; strong acids decompose it into metallic copper and binoxide of copper, which, on contact with these acids, gives a salt of copper.

$$\underset{\substack{\text{Oxide of}\\ \text{copper.}}}{\left(Cu^2O\right)} + \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2''}\\ H^2\end{matrix}\right\} O^2\right)} = \underset{\text{Copper.}}{Cu''} + \underset{\substack{\text{Sulphate of}\\ \text{copper.}}}{\left(\left.\begin{matrix}SO^{2''}\\ Cu''\end{matrix}\right\} O^2\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\} O\right)}$$

Ammonia dissolves this oxide without becoming coloured, but the solution turns blue by absorbing oxygen when exposed to the air.

**Distinctive Characters of the Salts of Copper.**—The salts of copper are recognized in analyses by the following properties:

1st. A sheet of iron plunged into a solution of a salt of this metal becomes covered with an adhesive coating of copper of a beautiful red colour.

2nd. Hydrosulphuric acid forms in these solutions a precipitate insoluble in alkaline sulphides, and which is not produced in presence of cyanide of potassium.

The per-salts may be distinguished from the sub-salts:

1st. With sub-salts, potash gives a yellow precipitate insoluble in an excess of the reagent. Per-salts are precipitated of a dirty blue colour by the same reagent, and the precipitate becomes black when boiled, provided that the potash has been added in sufficient quantity to decompose the whole of the salt of copper.

2nd. Ammonia produces in per- and sub-salts a precipitate soluble in an excess of the reagent; but with per-salts the ammoniacal solution is a beautiful blue, while with sub-salts this solution is colourless, and only turns blue on contact with air.

All the salts of copper are poisonous: the best antidote for poisoning by preparations of copper consists in administering a few whites of eggs and then giving an emetic. The albumen of the egg forms with the copper a compound, only very slightly soluble, and thus the absorption of the metal is prevented until the emetic acts.

It has been proposed to substitute iron filings for albumen, with the idea of precipitating the copper in a metallic state; or sulphide of iron, which should form sulphide of copper.

Copper enters into several common alloys. When united with zinc it constitutes brass; with tin it forms bronze; and we have seen that the silver used in money and jewellery is alloyed with copper.

## MERCURY Hg.

Atomic weight = 200. Molecular weight = 200.

Mercury is found native, but in too small quantity to be worked. It is chiefly extracted from the sulphide of mercury or cinnabar. The principal mines worked are at Almaden in Spain and at Idria in Illyria. Though the metallurgic processes employed vary a little in different places in the arrangement of apparatus, they are chemically reduced into a single one, which consists in roasting the ore. The sulphur passes to the state of sulphurous anhydride, and the mercury is liberated:

$$\begin{array}{ccccccc} \left(HgS\right) & + & \left.\begin{matrix} O \\ O \end{matrix}\right\} & = & \left(SO^2\right) & + & Hg \\ \text{Sulphide of mercury.} & & \text{Oxygen.} & & \text{Sulphurous anhydride.} & & \text{Mercury.} \end{array}$$

Mercury may also be displaced from its sulphide by heating the latter with iron.

$$\begin{array}{ccccccc} (HgS) & + & Fe & = & (FeS) & + & Hg \\ \text{Sulphide of mercury.} & & \text{Iron.} & & \text{Sulphide of iron.} & & \text{Mercury.} \end{array}$$

The mercury obtained by these methods is filtered through wash-leather and placed in iron bottles.

In order to obtain the metal pure, it must be treated by a quantity of nitric acid insufficient to dissolve it, and the whole left for twenty-four hours. Nitrate of mercury is first formed, and other metals are afterwards substituted for the mercury of this nitrate. After twenty-four hours all these metals become dissolved, and the portion of mercury not acted on remains in a state of absolute purity.

Mercury is liquid at the ordinary temperature; it is solidified at −40° and boils at 350°. In the solid state this metal is of a silver whiteness; it is malleable, and crystallizes in octahedra; its density is 14·4; its density in the liquid state is 13·59, and its vapour density is 6·976.

Pure mercury does not adhere to porcelain or glass, but adheres to these substances if alloyed with lead or other metals, and assumes the form of small elongated drops.

Mercury oxidizes slowly in the air. This oxidation becomes much more active at a temperature of about 350°. It also takes place in the cold very readily in presence of ozonized oxygen. It is not acted on by hydrochloric acid. Nitric acid rapidly dissolves it: when cold, and in presence of an excess of metal, sub-nitrate of mercury is formed; when hot, and with an excess of acid, per-nitrate is produced. Boiling sulphuric acid dissolves mercury, disengaging sulphurous anhydride. According to whether the acid or the metal predominate, the sulphate formed is per- or sub-sulphate.

In presence of air and acids, alkaline chlorides cause mercury to pass to the state of chloride. The absorption of this metal by the skin is explained by this reaction.

Chlorine, bromine, and iodine combine directly with mercury in the cold. Sulphur also can enter into direct combination with this metal. Mercurial compounds capable of absorption act as poisons on the animal economy. Workmen who breathe mercurial vapours are generally affected by a remarkable tremulous state known as mercurial palsy.

In medicine, mercurial compounds are employed with success in syphilis, inflammation of the membranes, etc., etc.

Mercury, like copper, is biatomic, and its atoms, like those of copper, possess the property of combining with each other, losing one part only of their capacity for saturation. The result is, that not only the atom Hg, but even the group $Hg^2$ acts as a biatomic radicle and can enter into combination with different radicles.

Compounds into which the atom Hg enters are called per-compounds, and those into which the group $Hg^2$ enters take the name of sub-compounds.

The principal per-compounds are:

| | |
|---|---|
| The bichloride of mercury . . . . | $HgCl^2$ |
| The bibromide . . . . . . . . | $HgBr^2$ |

| | |
|---|---|
| The biniodide . . . . . . . . | $HgI^2$ |
| The bifluoride . . . . . . . . | $HgFl^2$ |
| The peroxide . . . . . . . . | $HgO$ |
| The persulphide . . . . . . . | $HgS$ |

and the per-salts resulting from the replacement of the basic hydrogen of acids by the biatomic atom Hg.

The principal sub-compounds are:

| | |
|---|---|
| The protochloride of mercury . . | $Hg^2Cl^2$ |
| The protobromide . . . . . . . | $Hg^2Br^2$ |
| The prot-iodide . . . . . . . | $Hg^2I^2$ |
| The sub-oxide or oxydule . . . . | $Hg^2O$ |
| The sub-sulphide . . . . . . . | $Hg^2S$ |

and the sub-salts which result from the substitution of the biatomic radicle $Hg^2$ for the typical hydrogen of acids.

### PER-COMPOUNDS OF MERCURY (MERCURIC COMPOUNDS).

**Perchloride of Mercury** $\left(Hg''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)$.—The bichloride of mercury (corrosive sublimate) may be obtained either by the action of chlorine on mercury, or by the distillation of a mixture of common salt and persulphate of mercury.

$$\text{1st.}\quad \underset{\text{Mercury.}}{Hg''} + \underset{\text{Chlorine.}}{\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}} = \underset{\text{Mercuric chloride.}}{\left(Hg''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)}$$

$$\text{2nd.}\quad \underset{\text{Mercuric sulphate.}}{\left(\left.\begin{matrix}SO^{2''}\\Hg''\end{matrix}\right\}O^2\right)} + \underset{\text{Chloride of sodium.}}{2\left(\left.\begin{matrix}Na\\Cl\end{matrix}\right\}\right)} = \underset{\text{Sulphate of sodium.}}{\left(\left.\begin{matrix}SO^{2''}\\Na^2\end{matrix}\right\}O^2\right)} + \underset{\text{Corrosive sublimate.}}{\left(Hg''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)}$$

This distillation takes place in a large globe heated by a sand-bath (fig. 35); the bichloride is sublimed and deposited on the cold upper part of this vase.

As the mercuric almost always contains a little mercurous sulphate, which would give protochloride ($Hg^2Cl^2$) on reacting with chloride of sodium, when this second method is employed a little binoxide of manganese is added to the mixture. On contact with the chloride of sodium and the excess of acid contained in the mercuric sulphate, this binoxide gives rise to a slight disengagement of chlorine, which causes the small quantity of protochloride formed to pass to the state of bichloride.

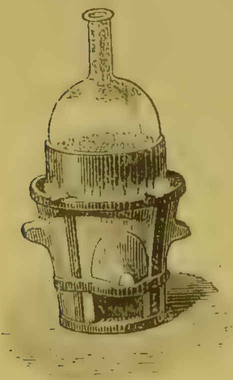


Fig. 35.

LEEDS SCHOOL OF MEDICINE

$$\underset{\text{Protochloride of mercury.}}{\left(Hg^2Cl^2\right)} + \underset{\text{Chlorine.}}{\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}} = \underset{\text{Bichloride of mercury.}}{2\left(Hg''Cl^2\right)}$$

Bichloride of mercury is dissolved in greater proportion in boiling water than in cold. Alcohol dissolves it better than water, and ether better than alcohol; its alcoholic solution leaves it, by evaporation, crystallized in right prisms having a rhomboid base; by sublimation it crystallizes in rectangular octahedra; its density is 6·5, its fusing point is 265°, its boiling point is 295°, and its vapour density 9·42.

On causing a reducing body such as protochloride of tin, to act on a solution of corrosive sublimate, a white precipitate of protochloride of mercury is obtained; if the mixture be boiled, the protochloride is reduced to the state of metallic mercury.

When a solution of corrosive sublimate is poured into ammonia, a white precipitate is formed which is called amido-chloride of mercury, and which has for formula $\left(\left.\begin{matrix}Hg''\\Hg''\\H^4\end{matrix}\right\} N^2,Cl^2\right)$

If, on the contrary, ammonia be poured into the solution of sublimate, an equally white body precipitates whose formula is $((HgCl^2)^3,Hg''H^4N^2)$ : this latter body may be regarded as a combination of bichloride and amide of mercury.

Albumen gives an insoluble precipitate with the sublimate, the composition of which is not well understood, and appears to vary with the time it has been kept.

Corrosive sublimate has a great tendency to form double chlorides with alkaline chlorides. The sodium salt has for formula $\left.\begin{matrix}Hg''\\Cl^2\end{matrix}\right\}, 2\left(\left.\begin{matrix}Na\\Cl\end{matrix}\right\}\right)$.

Corrosive sublimate is a violent poison, the best antidote for which consists in administering whites of eggs, and then an emetic. The albumen rendering the sublimate insoluble, arrests its absorption until the emetic acts. The action of corrosive sublimate on albumen makes this salt useful for the preservation of animal matters.

Corrosive sublimate is one of the compounds used as basis for the pharmaceutical mercurial preparations.

**Mercuric Bromide** $\left(Hg''\left\{\begin{matrix}Br\\Br\end{matrix}\right.\right)$.—Mercuric bromide is prepared by the same methods as the chloride and possesses analogous properties.

**Biniodide of Mercury** $\left(Hg''\left\{\begin{matrix}I\\I\end{matrix}\right.\right)$ may be prepared either directly, or by double decomposition. To prepare it directly 200 parts of mercury are triturated in a mortar with 254 parts of iodine; to facilitate the operation a little alcohol is added, and the trituration is continued until the mass assumes a beautiful red colour and until no globule of metallic mercury can be distinguished by a magnifying glass.

By double decomposition, an aqueous solution of 318 parts of iodide of potassium are poured into an aqueous solution of 271 parts of corrosive sublimate; a beautiful orange-red precipitate forms, which is the biniodide of mercury.

$$\underset{\substack{\text{Bichloride of}\\\text{mercury.}}}{\left(Hg''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)} + \underset{\substack{\text{Iodide of}\\\text{potassium.}}}{2\left(\left.\begin{matrix}K\\I\end{matrix}\right\}\right)} = \underset{\substack{\text{Chloride of}\\\text{potassium.}}}{2\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)} + \underset{\substack{\text{Biniodide of}\\\text{mercury.}}}{\left(Hg''\left\{\begin{matrix}I\\I\end{matrix}\right.\right)}$$

If, instead of employing the atomic proportions we have just indicated, an excess of either reagent were used, the precipitate would again dissolve.

When biniodide of mercury is dissolved in a boiling solution of iodide of potassium, part of it is deposited crystallized on cooling; the crystals thus obtained are red.

Biniodide of mercury is sufficiently volatile to be sublimed; in this case yellow crystals are deposited, which become red if pulverized: heat is disengaged during this latter transformation. The yellow crystals of biniodide of mercury belong to the fourth crystalline system, while the red ones belong to the second; this salt is therefore dimorphous.

The biniodide of mercury is principally used in medicine for outward applications, nevertheless it is contained in some preparations that are taken internally.

Biniodide of mercury combines with alkaline iodides; the formula of these double iodides is:

$$\left(\left.\begin{matrix}Hg''\\I^2\end{matrix}\right\}, 2\left(\left.\begin{matrix}M\\I\end{matrix}\right\}\right)\right)$$

**Mercuric Sulphide** ($Hg''S$).—This substance may be prepared by heating sulphur and mercury together, or by precipitating a per-salt of mercury by sulphuretted hydrogen.

$$\underset{\substack{\text{Bichloride of}\\\text{mercury.}}}{\left(Hg''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}S\right)} = \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\substack{\text{Mercuric}\\\text{sulphide.}}}{\left(Hg''S\right)}$$

In the latter case, the sulphide of mercury forms a black mass. This mass, dried and heated in globes with open necks, is volatilized and deposited on the cold parts of these globes in reddish-violet crystals. These crystals are identical with those found native, and like these latter they are called cinnabar. The mercuric sulphide is therefore dimorphous like the iodide; it volatilizes at an elevated temperature without decomposing if the operation be conducted without exposure to the air; in a current of air it is converted into mercury and sulphurous anhydride.

$$\underset{\substack{\text{Sulphide of}\\\text{mercury.}}}{\left(Hg''S\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} = \underset{\substack{\text{Sulphurous}\\\text{anhydride.}}}{\left(SO^2\right)} + \underset{\text{Mercury.}}{Hg''}$$

The density of natural cinnabar is 8·1, and that of artificial cinnabar may descend to 7·65. The crystals of cinnabar deviate the plane of polarized light to the left; it is very possible that some day crystals of the same substance may be found which will be dextrogyrate.

There is one variety of mercuric sulphide which is of a much purer red than cinnabar. This variety is known as vermilion, and is prepared by triturating for several hours a mixture composed of

| | |
|---|---|
| Mercury . . . . . . . . . . . | 300 parts. |
| Sulphur . . . . . . . . . . . | 114 ,, |
| Water . . . . . . . . . . . | 400 ,, |
| Potash . . . . . . . . . . . | 75 ,, |

The mass which forms is black, but it becomes a beautiful red after exposure for some time to a temperature of 50°.

The beautiful shade of vermilion is attributed to the action of the alkaline sulphide which forms in the reaction. Vermilion and cinnabar are used in painting.

**Mercuric Oxide.**—There are two varieties of oxide, as of sulphide and iodide of mercury; one of these is yellow and the other red. The yellow oxide of mercury is obtained by precipitating a mercuric salt by a soluble base.

$$\underset{\text{Chloride of mercury.}}{\left(\mathrm{Hg}''\left\{\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right.\right)} + \underset{\text{Potash.}}{2\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\text{Chloride of potassium.}}{2\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\text{Mercuric oxide.}}{\left(\mathrm{Hg}''\mathrm{O}\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}$$

The precipitate thus obtained is anhydrous: it is collected on a filter, washed and dried.

The red oxide may be prepared either by heating mercury in air, or by slightly calcining per- or sub-nitrate of mercury; the oxide obtained by means of the pernitrate is redder than that arising from the calcination of the subnitrate.

The process by heating mercury in air is no longer employed. It is from it that the name of *precipitate per se* was applied to the binoxide of mercury.

Mercuric oxide decomposes at 400°; so that, between the temperature at which the metal oxidizes and that at which it is reduced, the difference is scarcely more than 50°.

One part of this oxide appears to dissolve in 20,000 to 30,000 parts of water: the solution does not affect litmus; but if sea salt be added, chloride of mercury and hydrate of sodium form, and a strongly-alkaline reaction is then manifested.

Blue light seems to reduce the binoxide of mercury, but white light does not alter it.

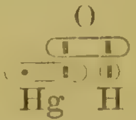
The yellow oxide, when left in a bottle with ammonia, combines with the elements of this body without changing colour: the product thus formed is a powerful base which combines with acids without decomposition, forming well-defined salts. These salts have received the name of ammonio-mercuric salts. The base answers to the formula

$$(Hg''O)^3N^2Hg''H^4 \quad + \quad 3(H^2O)$$

By admitting that the water it contains is water of crystallization, the ammonio-mercuric oxide may be represented by the following formula:

$$\left(\left.\begin{matrix} Hg'' \\ (Hg''OH)' \\ (Hg''OH)' \\ (Hg''OH)' \\ H' \end{matrix}\right\} N^2 + 3\,aq.\right)$$

This would be an ammonia twice condensed, in which biatomic Hg'' would take the place of $H^2$, and in which 3H would be replaced three times by the monatomic residue (Hg''OH).



$= (Hg''OH)'$

**Per-Nitrate of Mercury** $\left(Hg''\left\{\begin{matrix}ONO^2\\ONO^2\end{matrix}\right.\right)$.—When mercury is dissolved in an excess of boiling nitric acid, and the concentrated liquid is evaporated spontaneously in vacuo, crystals of basic per-nitrate of mercury form, and the liquid retains in solution the uncrystallizable neutral nitrate of mercury; water precipitates another basic nitrate from this liquid.

**Per-Sulphate of Mercury** $\left(\left.\begin{matrix}SO^{2''}\\Hg''\end{matrix}\right\}O^2\right)$.—This salt is prepared by causing an excess of boiling sulphuric acid to act on metallic mercury. The salt is deposited in the form either of a crystalline powder or in small needles. Water decomposes it, forming a basic salt known as turpeth mineral, which when boiled for a long time in water loses the elements of sulphuric anhydride and leaves a residue of binoxide of mercury. The formula of turpeth mineral is:

$$\left(\left.\begin{matrix} SO^{2''} \\ \left(\begin{matrix} Hg \\ Hg \\ Hg \end{matrix}\begin{matrix} \}\,O \\ \\ \}\,O \end{matrix}\right)'' \end{matrix}\right\} O^2\right)$$

## MERCUROUS COMPOUNDS.

**Protochloride of Mercury (Calomel)** $(Hg^2Cl.)$ — Protochloride of mercury may be obtained either by triturating the bichloride with mercury, or by distilling the subsulphate of mercury with chloride of sodium.

1st. $\underset{\text{Bichloride of mercury.}}{(Hg''Cl^2)} + \underset{\text{Mercury.}}{Hg''} = \underset{\text{Protochloride of mercury.}}{(Hg^2Cl^2)}$

$$\text{2nd.}\quad \underset{\text{Subsulphate of mercury.}}{\left(\left.\begin{matrix}SO^{2''}\\Hg^{2''}\end{matrix}\right\}O^2\right)} + 2\underset{\text{Chloride of sodium.}}{\left(\left.\begin{matrix}Na\\Cl\end{matrix}\right\}\right)} = \underset{\text{Sulphate of sodium.}}{\left(\left.\begin{matrix}SO^{2''}\\Na^2\end{matrix}\right\}O^2\right)} + \underset{\text{Mercurous chloride.}}{\left(Hg^2Cl^2\right)}$$

This salt may also be prepared by precipitating a soluble sub-salt of mercury by hydrochloric acid, or by a chloride dissolved in water.

$$\underset{\text{Mercurous nitrate.}}{\left(Hg^{2''}\left\{\begin{matrix}ONO^2\\ONO^2\end{matrix}\right.\right)} + 2\underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\text{Mercurous chloride.}}{\left(Hg^2Cl^2\right)} + 2\underset{\text{Nitric acid.}}{\left(NHO^3\right)}$$

When calomel is distilled, and its vapour received into an apparatus full of air, this fluid is interposed between the molecules at the time of their solidification, and a powder precipitates which is called vaporized calomel, because formerly vapour of water was substituted for air in this operation.

Calomel acts as a purgative, and when given in small, and often-repeated doses, it occasions mercurial salivation.

Mercurous chloride crystallizes by sublimation in prisms having a square base and terminated by octahedral points. These prisms belong to the second system. The protochloride of mercury is white; it decomposes into mercury and corrosive sublimate when exposed to light.

$$\underset{\text{Protochloride of mercury.}}{(Hg^2Cl^2)} = \underset{\text{Corrosive sublimate.}}{(HgCl^2)} + \underset{\text{Mercury.}}{Hg}$$

A similar decomposition appears to take place when it is vaporized; calomel is, in fact, one of those bodies the vapour densities of which seem to be exceptions to Ampère's law, its density being half what it ought to be. This anomaly is explained, like that of the chloride of ammonium, by admitting that dissociation takes place.

Calomel is insoluble in water, alcohol, or ether.

Nitric and hydrochloric acids attack it. By nitric acid it is converted into a mixture of bichloride and per-nitrate; while by hydrochloric acid it is wholly converted into bichloride.

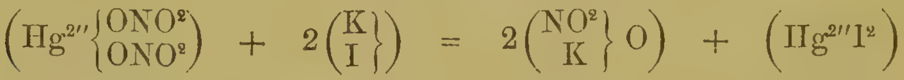
When heated with alkaline chlorides, calomel is transformed into corrosive sublimate. This action can even be produced at 38° or 40°, if organic matters intervene, especially in presence of acids and the oxygen of the air. This is a very important fact: the stomach always containing acids, air, and organic matters, we must avoid giving alkaline chlorides at the same time as calomel, or there may be danger of producing the poisonous sublimate in the stomach.

On contact with ammonia, calomel is transformed into a black substance answering to the formula

$$\left(\left.\begin{matrix}Hg^{2''}\\Hg^{2''}\\H^4\end{matrix}\right\}N^2Cl^2\right) = \left(Hg^4N^2H^4,Cl^2\right)$$

**Protobromide of Mercury** ($Hg^{2''}Br^2$) is prepared like the protochloride, and possesses analogous properties; it is not used.

**Prot-iodide of Mercury** ($Hg^{2''}I^2$.—This salt may be obtained by precipitating mercurous nitrate by iodide of potassium.



$$\left(Hg^{2''}\left\{\begin{matrix}ONO^2\\ONO^2\end{matrix}\right.\right) + 2\left(\begin{matrix}K\\I\end{matrix}\right\}\right) = 2\left(\begin{matrix}NO^2\\K\end{matrix}\right\} O\right) + \left(Hg^{2''}I^2\right)$$

Mercurous nitrate. Iodide of potassium. Nitrate of potassium. Prot-iodide of mercury.

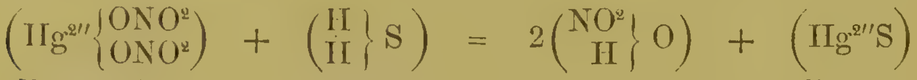
But, as mercurous nitrate is always acid, iodine is liberated during the reaction, and this iodine causes one portion of the prot-iodide to pass to the state of biniodide.

In order to obtain the prot-iodide pure, it is better to triturate 200 parts of mercury with 127 parts of iodine under alcohol.

The prot-iodide of mercury is greenish-yellow. When suddenly heated it volatilizes without decomposing; when slowly heated, on the contrary, it abandons half its metal, and passes to the state of biniodide.

The prot-iodide of mercury is insoluble in water, alcohol, or ether; heated with alkaline iodides, it gives mercury, at the same time forming biniodide, and consecutively a double iodide.

**Subsulphide of Mercury** ($Hg^2S$).—This body is very instable; it is formed when a soluble mercurous salt is precipitated by hydrosulphuric acid.



$$\left(Hg^{2''}\left\{\begin{matrix}ONO^2\\ONO^2\end{matrix}\right.\right) + \left(\begin{matrix}H\\H\end{matrix}\right\} S\right) = 2\left(\begin{matrix}NO^2\\H\end{matrix}\right\} O\right) + \left(Hg^{2''}S\right)$$

Mercurous nitrate. Hydrosulphuric acid. Nitric acid. Mercurous sulphide.

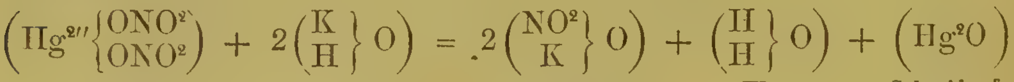
But it decomposes almost immediately into metallic mercury and mercuric sulphide.

$$(Hg^{2''}S) = Hg + (Hg''S)$$

Subsulphide of mercury. Mercury. Mercuric sulphide.

The subsulphide of mercury is of a black colour.

**Suboxide of Mercury** ($Hg^{2''}O$).—The suboxide is a black powder obtained by precipitating the subnitrate by potash:



$$\left(Hg^{2''}\left\{\begin{matrix}ONO^2\\ONO^2\end{matrix}\right.\right) + 2\left(\begin{matrix}K\\H\end{matrix}\right\} O\right) = 2\left(\begin{matrix}NO^2\\K\end{matrix}\right\} O\right) + \left(\begin{matrix}H\\H\end{matrix}\right\} O\right) + \left(Hg^2O\right)$$

Subnitrate of mercury. Potash. Nitrate of potassium. Water. Suboxide of mercury.

It is quite as instable as the subsulphide, and decomposes in the same manner, that is to say, into mercury and mercuric oxide.

$$(Hg^{2''}O) = (Hg''O) + Hg$$

Suboxide of mercury. Mercuric oxide. Mercury.

**Mercurous Nitrate** $\left(\begin{matrix}(NO^2)^2\\Hg^{2''}\end{matrix}\right\} O^2\right)$.—This is prepared by leaving mercury in an excess of cold dilute nitric acid. After a short time beautiful crystals deposit, which are derived from an oblique rhomboid prism. This salt dissolves in a small quantity of water; if the water be in excess, a basic salt is precipitated, and part of the neutral salt remains dissolved by means of the nitric acid liberated.

If the dilute nitric acid be left with a great excess of mercury in the cold, a condensed salt is formed, which presents large colourless crystals; the formula of this salt is:

$$\left(\begin{array}{ll} \mathrm{Hg}^{2\prime\prime} & \mathrm{ONO}^{2} \\ \mathrm{Hg}^{2\prime\prime} & \}\mathrm{O} \\ \mathrm{Hg}^{2\prime\prime} & \}\mathrm{O} \\ & \mathrm{ONO}^{2} \end{array}\right)$$

**Subsulphate of Mercury** $\left(\left.\begin{matrix}\mathrm{SO}^{2\prime\prime} \\ \mathrm{Hg}^{2\prime\prime}\end{matrix}\right\} \mathrm{O}^{2}\right)$.—This salt is only used in the preparation of calomel; in order to obtain it, mercury is converted into persulphate, which is then triturated with a quantity of the metal equal to that already employed.

**Analytic Reactions of Mercurial Salts.**—These salts are recognized by the following characters:

1st. With hydrosulphuric acid they give a black precipitate, which is insoluble in sulphide of ammonium and in boiling nitric acid.

2nd. A sheet of copper causes a deposit of mercury with which it is amalgamated, becoming white. It regains its original colour when heated so as to vaporize the mercury. If the operation be conducted so that the vapours are condensed, quicksilver can be obtained.

The following characteristics distinguish per-salts of mercury from sub-salts of the same metal:

1st. Caustic alkalies and ammonia in the solutions of sub-salts form a black precipitate of sub-oxide of mercury, which decomposes almost instantaneously into mercury and mercuric oxide:

$$\underset{\text{Sub-oxide of mercury.}}{(\mathrm{Hg}^{2}\mathrm{O})} = \underset{\text{Mercuric oxide.}}{(\mathrm{HgO})} + \underset{\text{Mercury.}}{\mathrm{Hg}}$$

Per-salts, on the contrary, with alkalies, give a yellow precipitate of the mercuric oxide, which is stable at the ordinary temperature.

2nd. Soluble chlorides and hydrochloric acid cause the formation of a white precipitate of protochloride of mercury in the solutions of sub-salts, and do not affect those of the per-salts.

3rd. Soluble iodides with sub-salts give a greenish-yellow precipitate of prot-iodide, while with per-salts they give an orange-red precipitate soluble in an excess of the mercurial salt or of the alkaline iodide.

LEEDS SCHOOL OF MEDICINE

## GENERAL REMARKS ON THE BIATOMIC METALS.

The biatomicity of the metals just spoken of is only manifested if we allow them the atomic weights which we have assigned to them. If, on the contrary, the old atomic weights were used, the biatomicity of these metals would disappear; hence it is of great importance that our actual atomic weights should be established on a firm basis.

These atomic weights are all based upon the great laws previously explained. All methods give corresponding results which corroborate each other.

1st. These atomic weights are all deduced from Dulong and Petit's law on specific heat, and this without any exception.

2nd. With the organic radicle ethyl, mercury forms a compound which evidently contains two molecules of ethyl, seeing that the half, and never less than the half, of this radicle can be replaced by chlorine, bromine, or iodine.

Moreover, if after having substituted chlorine, bromine, or iodine, for one molecule of ethyl, a second atom of these simple bodies be substituted for the second molecule of this compound radicle, we obtain chloride, bromide, or iodide of mercury, in which we thus find ourselves constrained to admit two atoms of chlorine, bromine, or iodine. This conclusion is also confirmed by the vapour density of bichloride of mercury, and by the molecular weight thence deduced for this compound.

The bichloride of mercury gives rise to very distinct double decompositions, in which other mercurial compounds of the same degree, such as the peroxide and per-salts, are produced. In all these compounds it is always the same quantity of mercury which enters into the reaction.

It is true that it is possible to transform the bichloride of mercury into protochloride. But in this transformation a body is obtained in which at least the same quantity of mercury, and probably double the quantity, acts.

It results from these facts that the smallest quantity of mercury that can be transferred from one combination to another by means of double decomposition is equal to 200, or, in other words, that 200 is the atomic weight of mercury.

3rd. Copper forms two degrees of combination which present the strictest relations with the mercurial compounds of the same order. We thence conclude that these compounds have the same formula as those of mercury. Hence the bichloride of copper ought to be written ($CuCl^2$), and from this formula the atomic weight 63 for copper is deduced.

4th. The sulphate of copper is capable of forming double sulphates with alkaline sulphates. These double sulphates are isomorphous with the salts of the same nature having for base cadmium, zinc, magnesium, strontium, barium, and probably calcium, though at present experimental proof is wanting for the latter metal: all these salts crystallize with six molecules of water.

The salts of the preceding metals are also isomorphous with other salts, such as the simple sulphates, which crystallize sometimes with seven, sometimes with five molecules of water, and which present the same forms when they contain the same quantity of water. With many of them isomorphism is observed between their carbonates, chlorates, bromates, tungstates, etc.

From the isomorphism existing between the compounds of the different metals we have named, we must conclude, according to Mitscherlich's law, that these compounds ought to be represented by similar formulæ, from which the atomic weights we have adopted for these metals are deduced, and which are in accord with their capacity for heat. Thus the conclusions drawn from the vapour densities, those drawn from Dulong and Petit's law, those drawn from Mitscherlich's law, and those based on chemical resemblances, all concur in making us believe that the new atomic weights, as well as the biatomicity of the metals we have just studied, are correct.

Owing to the isomorphism of the compounds of magnesium with those of copper, cadmium, zinc, calcium, barium, and strontium, the term magnesian series has been applied to these metals, and certain tetratomic metals, such as manganese, iron, nickel, and cobalt, have been added to this series. These latter bodies form non-saturated sub-compounds, which are represented by the same formulæ as those of the preceding metals, and are isomorphous with them. Nevertheless, these four metals being completely separated from the others by their per-compounds, ought to be placed in a different group; their isomorphism with the true magnesian metals is not the less in favour of the formulæ by which their sub-compounds are represented, and consequently of the atomic weights thence deduced.

## THIRD CLASS (TRIATOMIC METALS.)

This class contains gold, vanadium, and thallium. Gold alone has sufficient importance to require our notice.

### GOLD $\left.\begin{matrix}Au'''\\Au'''\end{matrix}\right\}$

Atomic weight = 196·5. Probable molecular weight = 393·0.

Gold is found native; sometimes crystallized regularly in cubes or in octahedra, sometimes in isolated masses which are called nuggets; occasionally it is pure, but generally it is alloyed with silver, platinum, rhodium, etc.

Metallic mercury is made to act on the ore, and the gold and silver are thereby dissolved: on distilling the amalgam, an alloy of these two latter metals is obtained; and this alloy, when heated for twenty-four or thirty hours with a mixture of sea salt and brick-dust, loses almost the whole of its silver. The silver passes to the state of chloride, whence it is extracted by the processes which we have described. It is probable that in this operation the silica acts on the sea salt at the same time as the atmospheric moisture, and that hydrochloric acid is produced, which causes the silver to pass to the state of chloride.

The best method of obtaining perfectly pure gold consists in preparing the chloride by dissolving this metal in aqua regia, and pouring a solution of proto-sulphate of iron and a little hydrochloric acid into the solution of the salt; very pure gold precipitates in the form of a brown powder, which may be aggregated by fusion.

Gold is yellow, or, rather, red when the light is reflected several times on its surface before reaching the eye; when seen by transmitted light it has a green shade.

Aqua regia easily dissolves it when hot; selenic acid also attacks it, but no other acid has any action on it. Chlorine and bromine act upon it even cold.

Gold melts at about 1100°; its density is 19·5; it is the most malleable and the most ductile of all metals; its tenacity is less than that of iron, copper, platinum, or silver. It is very soft, but may be hardened by hammering: in order to facilitate its working, it is usually alloyed either with silver or copper.

Gold being triatomic may combine either with three monatomic atoms, forming a saturated compound, or with only one of these atoms, giving a non-saturated compound. We know:

| | |
|---|---|
| The protochloride of gold . . . . . . . | $AuCl$. |
| The prot-iodide of gold . . . . . . . . . | $AuI$. |
| The perchloride of gold . . . . . . . . . | $Au'''Cl^3$. |
| The perbromide of gold . . . . . . . . . | $Au'''Br^3$, etc. |

As an uneven number of atoms of chlorine could not be replaced by oxygen and biatomic bodies in general, two atoms of gold intervene in the oxides and sulphides of this metal. We know:

| | |
|---|---|
| A protoxide of gold . . . . . . | $\left.\begin{matrix}Au\\Au\end{matrix}\right\}O$ |
| And a sesquioxide . . . . . . | $\left.\begin{matrix}Au\\Au\end{matrix}\right\}O^3$ |
| A protosulphide of gold . . . . . | $\left.\begin{matrix}Au\\Au\end{matrix}\right\}S$ |
| And a sesquisulphide. . . . . . | $\left.\begin{matrix}Au\\Au\end{matrix}\right\}S^3$ |

**Perchloride of Gold** $\left(Au'''\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right.\right)$.—The perchloride of gold is prepared by dissolving the pure metal in aqua regia, and then evaporating by the water-bath; if the operation be arrested as soon as the cooled liquid commences to give crystals, needles deposit, which are a compound of hydrochloric acid and chloride of gold. If, on the contrary, the heat be continued until the evaporation is complete, a yellow melted matter is obtained, which on cooling forms crystalline needles.

At 160°, the perchloride of gold loses two-thirds of its chlorine, and is transformed into the protochloride, insoluble in water; above 200°, this protochloride is itself reduced, and there remains metallic gold.

Perchloride of gold is very soluble in water, to which it gives a beautiful yellow colour: on shaking this solution with ether, the latter becomes coloured, taking up the chloride of gold, while the water regains its original colour. The perchloride of gold is therefore still more soluble in ether than in water. Light slowly decomposes it: metallic gold is deposited on the sides of vessels containing this salt. Reducing bodies such as proto-salts of iron, oxalic acid, etc., also decompose the perchloride of gold, liberating the metal:

$$\underset{\substack{\text{Perchloride}\\\text{of gold.}}}{2\left(Au'''Cl^3\right)} + \underset{\text{Sulphate of iron.}}{6\left(\left.\begin{matrix}SO^{2''}\\Fe''\end{matrix}\right\}O^2\right)} + \underset{\text{Water.}}{6\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

$$= \underset{\substack{\text{Basic persulphate}\\\text{of iron.}}}{3\left(\left.\begin{matrix}(SO^{2''})^2\\Fe^{2\text{vi}}\\H^2\end{matrix}\right\}O^6\right)} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{6\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Gold.}}{\left.\begin{matrix}Au'''\\Au'''\end{matrix}\right\}}$$

$$\underset{\substack{\text{Perchloride of}\\\text{gold.}}}{2\left(AuCl^3\right)} + \underset{\text{Oxalic acid.}}{3\left(\left.\begin{matrix}C^2O^{2''}\\H^2\end{matrix}\right\}O^2\right)} = \underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{6\left(CO^2\right)} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{6\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Gold.}}{\left.\begin{matrix}Au'''\\Au'''\end{matrix}\right\}}$$

When perchloride of gold is reduced by means of the protochloride of tin, the precipitate which forms is not pure gold; it contains gold, tin, and oxygen, and is called purple of Cassius.

The reduction of chloride of gold by the skin stains this latter violet.

Chloride of gold forms double chlorides with the other metallic chlorides; those which contain alkaline metals are the best defined; their formulas are:

$(Au'''Cl^3,KCl + 5\ aq.)$ = chloride of gold and potassium.
$(Au'''Cl^3,NaCl + 4\ aq.)$ = chloride of gold and sodium.
$(Au'''Cl^3,NH^4Cl + 2\ aq.)$ = chloride of gold and ammonium.

These chlorides are either molecular combinations, or their chlorine acts as trivalent.

With the aqueous solution of perchloride of gold, ammonia gives an explosive precipitate (detonating gold) containing chlorine, hydrogen, nitrogen, oxygen, and gold.

When left for some time in contact with ammonia, this compound loses all its chlorine and becomes still more explosive. Its formula then appears to be

$$(Au^2O^3, N^2H^6, H^2O)$$

**Perbromide of Gold** ($Au'''Br^3$).—This is obtained like the perchloride, that is to say, by dissolving gold in an aqua regia made with nitric and hydrobromic acids; its properties are similar to those of the chloride.

**Prot-iodide of Gold** ($Au'''I$).—The periodide of gold is not known; a prot-iodide of this metal is obtained by double decomposition.

**Sesquioxide of Gold** ($Au^2O^3$).—When an alkaline hydrate is poured into the solution of chloride of gold, no precipitate forms; but if the mixture be boiled, and then saturated with acetic acid, a precipitate is produced which, when properly dried, answers to the formula ($Au^2O^3$).

Sesquioxide of gold dissolves in hydrochloric and hydrobromic acids, giving rise to chloride and bromide of gold; hydrofluoric acid and the oxy-acids do not attack it, but it easily dissolves in alkaline hydrates. The sesquioxide of gold ought therefore to be considered as an acid anhydride.

The following equations explain the formation of this body:

$$\underset{\text{Perchloride of gold.}}{\left(Au'''Cl^3\right)} + \underset{\text{Potash.}}{6\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)}$$

$$\text{1st.} = \underset{\text{Chloride of potassium.}}{3\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)} + \underset{\text{Water.}}{3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Aurate of potassium.}}{\left(\left.\begin{matrix}Au'''\\K^3\end{matrix}\right\}O^3\right)}$$

$$\text{2nd.} \quad \underset{\text{Aurate of potassium.}}{\left(\left.\begin{matrix}Au'''\\K^3\end{matrix}\right\}O^3\right)} + \underset{\text{Acetic acid.}}{3\left(\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O\right)} = \underset{\text{Acetate of potassium.}}{3\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right)} + \underset{\text{Hydrate of gold.}}{\left(\left.\begin{matrix}Au'''\\H^3\end{matrix}\right\}O^3\right)}$$

$$\text{3rd.} \quad \underset{\text{Hydrate of gold.}}{2\left(\left.\begin{matrix}Au'''\\H^3\end{matrix}\right\}O^3\right)} = \underset{\text{Water.}}{3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Sesquioxide of gold, or auric anhydride.}}{\left(Au^2O^3\right)}$$

The aurate of potassium ($Au'''K^3O^3$) crystallizes with three molecules of water.

**Protoxide of Gold** ($Au^2O$).—This body remains under the form of an insoluble violet powder which can be decomposed at 250°, when the protochloride of gold is digested with the alkalies.

$$\underset{\text{Protochloride of gold.}}{2\left(AuCl\right)} + \underset{\text{Soda.}}{2\left(\left.\begin{matrix}Na\\H\end{matrix}\right\}O\right)} = \underset{\text{Chloride of sodium.}}{2\left(\left.\begin{matrix}Na\\Cl\end{matrix}\right\}\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Protoxide of gold.}}{\left(Au^2O\right)}$$

Protoxide of gold does not enter into double decomposition either with acids or bases. There is nevertheless a double hyposulphite of gold and sodium, the formula of which is:

$$\left(\left.\begin{matrix} S^2O'' \\ Na \\ Au' \end{matrix}\right\} O^2\right)$$

Gold here acts as monovalent, as it also does in all its sub-compounds.

In this compound the gold is so much concealed that neither sulphate of iron nor chloride of tin cause it to be manifested. When the solution of this hyposulphite is treated by chloride of barium, a double hyposulphite of gold and barium deposits, which, when treated by sulphuric acid, loses its barium and leaves hyposulphite of gold.

The double hyposulphite of gold and sodium is used to fix daguerrotype images.

**Sesquisulphide of Gold** ($Au^2S^3$) **and Protosulphide of Gold** ($Au^2S$).—When a current of hydrosulphuric acid is transmitted through a cold solution of perchloride of gold, the latter gives a yellow-brown deposit of sesquisulphide of gold. Under the same conditions, the boiling solution of perchloride of gold gives a precipitate of protosulphide.

These sulphides are true acid anhydrosulphides; they undergo very distinct double decompositions with the alkaline hydrosulphates, and are transformed into soluble sulpho-salts, disengaging hydrosulphuric acid.

$$\underset{\text{Sesquisulphide of gold.}}{\left(Au^2S^3\right)} + \underset{\text{Hydrosulphate of potassium.}}{6\left(\left.\begin{matrix} K \\ H \end{matrix}\right\} S\right)} = \underset{\text{Sulph-aurate of potassium.}}{2\left(\left.\begin{matrix} Au''' \\ K^3 \end{matrix}\right\} S^3\right)} + \underset{\text{Hydrosulphuric acid.}}{3\left(\left.\begin{matrix} H \\ H \end{matrix}\right\} S\right)}$$

**Reactions of Salts of Gold.**—Gold is recognized in analyses by the following properties:

1st. The perchloride of gold is deliquescent, but ether has a still greater affinity for it than water; if its solution in water be shaken with ether, the latter extracts the salt from the water.

2nd. Salts of gold are not precipitated by alkaline carbonates. The carbonate of ammonium produces a precipitate which easily detonates, and which is known as fulminating gold.

3rd. The salts of potassium and of sodium do not precipitate them.

4th. Protosulphate of iron reduces chloride of gold, especially if a little hydrochloric acid be added to the solution; the gold is then precipitated in the form of a brown powder.

5th. Salts of gold are freely precipitated by soluble iodides.

6th. The protochloride of tin produces a precipitate. When the solutions are dilute and the protochloride mixed with a little perchloride, this precipitate assumes a beautiful purple colour.

## FOURTH CLASS (TETRATOMIC METALS).

### ALUMINIUM Al.

Atomic weight = 275. Molecular weight unknown.

Aluminium may be obtained either by decomposing the anhydrous chloride of aluminium by sodium with the aid of heat, or by submitting a solution of the double chloride of aluminium and sodium to the action of an electric current. In both processes, the metal must afterwards be agglomerated by one or more fusions.

Aluminium has a white colour something between that of zinc and silver; it is very malleable, very ductile, and possesses very great tenacity. It is very sonorous, a good conductor of electricity, and melts at a temperature higher than that at which zinc fuses, and lower than silver. Its density is 2·56, which may be raised to 2·67 by pressure.

Aluminium does not oxidize directly at any temperature; it decomposes water at a white heat, producing alumina; nitric and sulphuric acids only attack it at the boiling temperature; hydrochloric acid dissolves it, on the contrary, with great ease.

Aluminium dissolves also in the solution of powerful bases such as potash or soda. In this case there is disengagement of hydrogen and the production of an alkaline aluminate.

Compounds of aluminium and carbon, and of aluminium and silicon, may be obtained, which compounds are analogous to cast iron.

Aluminium does not amalgamate with mercury; with copper it forms an alloy which possesses the property of welding at dull red heat, like iron.

There is no compound known into which aluminium enters as a single atom. Two atoms of this body always intervene in reactions. In consequence, we might be tempted to allow an atomic weight to aluminium double that we have admitted, but the isomorphism of the aluminic compounds with the per-compounds of iron leaves no doubt of the true formula of aluminic salts, and demonstrates the existence of the group $Al^2$.

Each atom of aluminium being tetratomic, and two atoms of any body whatsoever being unable to unite without exchanging at least two atomicities, the group $Al^2$ ought to be, and is, hexatomic.

Compounds are known which result from the combination of aluminium with monatomic radicles, such as chlorine, bromine, etc.: these compounds all correspond to the formula $(Al^{2''}R^6)$: combinations of aluminium with biatomic metalloids, such as oxygen and sulphur, are also known. They are represented by the general formula $(Al^2R''^3)$.

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## COMBINATIONS OF ALUMINIUM WITH MONATOMIC METALLOIDS.

**Chloride of Aluminium.**—This body is prepared by passing a current of dry chlorine over small porous pellets formed of oxide of aluminium and carbon, heated to redness.

$$\underset{\text{Oxide of aluminium.}}{(Al^2O^3)} + \underset{\text{Carbon.}}{3C} + \underset{\text{Chlorine.}}{3\left(\begin{matrix}Cl\\Cl\end{matrix}\right\}\Big)} = \underset{\text{Oxide of carbon.}}{3(CO)} + \underset{\text{Aluminic chloride.}}{\Big(\begin{matrix}Al^2\\Cl^6\end{matrix}\Big\}\Big)}$$

The operation is conducted in an apparatus similar to that used to prepare the chloride of silicon, the only difference being that, on account of the slight volatility of chloride of aluminium, the refrigerant apparatus is replaced by a receiver with a short neck connected by means of a socket with the neck of the retort in which the reaction takes place. The chloride is condensed in this vessel.

The porous mixture of aluminic oxide and carbon is obtained by calcining a paste made of oil, carbon, and oxide of aluminium: on mixing a sufficient quantity of chloride of sodium with this paste, instead of the chloride of aluminium the double chloride $((Al^2Cl^6), (NaCl)^2)$ is obtained, which is only used in the preparation of aluminium.

The chloride of aluminium crystallizes in colourless laminæ, which are sometimes transparent; it easily melts, and, according to Liebig, boils at 180°; in the air it gives off disagreeable fumes; it is deliquescent, and heat is disengaged when the salt is dissolved in water. The aqueous solution of this salt decomposes into hydrochloric acid and hydrate of aluminium when we attempt to evaporate it.

$$\underset{\text{Chloride of aluminium.}}{(Al^2Cl^6)} + \underset{\text{Water.}}{6\Big(\begin{matrix}H\\H\end{matrix}\Big\}O\Big)} = \underset{\text{Hydrochloric acid.}}{6\Big(\begin{matrix}H\\Cl\end{matrix}\Big\}\Big)} + \underset{\text{Hydrate of aluminium.}}{\Big(\begin{matrix}Al^2\\H^6\end{matrix}\Big\}O^6\Big)}$$

This prevents its being prepared by dissolving hydrate of aluminium in hydrochloric acid; but the hydrated chloride, which however cannot be desiccated, is obtained by this method.

**Fluoride of Aluminium** $(Al^2Fl^6)$.—M. Deville has obtained this body crystallized in cubes. He strongly heated oxide of aluminium previously moistened with hydrofluoric acid and then dried, in a tube of graphite protected externally by a stoneware tube: during the time the operation continues, a current of hydrogen ought to be transmitted through the tube, in order to carry over the vapours of the fluoride of aluminium, which is only volatile at white heat: at the end of the operation, beautiful crystals are found on the cold part of the tube.

The stoppers of the apparatus ought to be of charcoal, luted with a mixture of clay and cow's dung.

The fluoride of aluminium is insoluble in water. The strongest acids have no action on it.

## COMBINATIONS OF ALUMINIUM WITH BIATOMIC METALLOIDS.

**Oxide of Aluminium or Alumina** ($Al^2O^3$).—Alumina exists native, crystallized. Corundum is pure alumina, and sapphire and ruby are only alumina crystallized and coloured by traces of metallic oxides.

M. Deville has obtained these bodies by a very elegant process.

In a charcoal crucible he placed fluoride of aluminium; upon this body he placed a cupel full of boracic anhydride; he covered the crucible, placed it in a second earthen crucible, and kept it for an hour at a white heat; after this, on removing the crucible from the fire, and cooling, beautiful crystals of corundum were extracted.

In this operation, the boracic anhydride and fluoride of aluminium are mutually decomposed, forming alumina and fluoride of boron.

$$\underset{\text{Boracic anhydride.}}{(B^2O^3)} + \underset{\text{Fluoride of aluminium.}}{(Al^2Fl^6)} = \underset{\text{Fluoride of boron.}}{2(BFl^3)} + \underset{\text{Oxide of aluminium.}}{(Al^2O^3)}$$

Corundum crystallizes in the rhombohedral system. Amorphous alumina may be prepared by the calcination either of ammoniacal alum, or of hydrate of aluminium.

Alumina only fuses before the oxyhydrogen blow-pipe; it is in this manner that M. Gaudin obtained artificial rubies, differing only by their opacity from natural rubies: it is not attacked by alkaline solutions, and even concentrated acids only enter into double decomposition with it after a very long time: the corresponding hydrate acting either as acid or base, the oxide of aluminium is an indifferent anhydride.

**Hydrate of Aluminium** ($Al^2(OH)^6$).—This is obtained by precipitating a salt of aluminium by ammonia, collecting on a filter and well washing the precipitate produced. It may be precipitated by potash, but in that case it is difficult to wash, and the hydrate of aluminium obstinately retains traces of potash.

The hydrate of aluminium is capable of entering into double decomposition with acids, giving salts of aluminium resulting from the substitution of acid radicles for the typical hydrogen it contains. This hydrate also dissolves in alkaline solutions, giving aluminates. It therefore acts as base in presence of strong acids, and as an acid in presence of powerful bases.

Ammonia dissolves only a very small proportion of hydrate of aluminium; when its ammoniacal solution is left for some time in a stoppered bottle, microscopic crystals are deposited. Hydrate of aluminium exists native, and constitutes certain minerals, such as diaspore, gibbsite, and hydrargillite.

**Allotropic Modifications of Hydrate of Aluminium.**—When water holding hydrate of aluminium in suspension is boiled for twenty-four hours, this hydrate, without changing its composition, ceases to be soluble in acids and alkalies, and its properties therefore resemble those of the anhydride of aluminium

Besides this variety, Mr. Graham obtained soluble alumina by submitting an aqueous solution of aluminate of potassium to dialysis: potash alone passes through the membrane of the dialyser.

The soluble hydrate of aluminium appears only to be an allotropic modification of the ordinary hydrate; according to Mr. Graham, it constitutes a compound much more condensed.

**Double Sulphate of Aluminium and Potassium** (*Alum*) $\left(\left.\begin{matrix}SO^{2''}\\K^2\end{matrix}\right\}O^2, \left.\begin{matrix}(SO^{2''})^3\\Al^{2vi}\end{matrix}\right\}O^6 + 24\text{ aq.}\right)$.—In Italy and Hungary there is found a stone called alum-stone, which contains the elements of two molecules of sulphate of potassium, two molecules of sulphate of aluminium, and five molecules of hydrate of aluminium.

On heating this stone, the aggregation of its constituent principles is modified, and when lixiviated after the calcination, alum is dissolved, which is crystallized in cubes, and very pure. It is known in commerce as Roman alum.

Alum may be prepared artificially. To effect this, sulphuric acid is made to act on clay, which is a mixture of silicate of aluminium and silicate of iron, silica is deposited, and the sulphates of aluminium and iron enter into solution, sulphate of potassium is added to this, and on crystallizing, the alum is separated from the sulphate of iron, which does not readily crystallize. The alum thus prepared always contains a little iron, which affects its colour: it is crystallized in octahedra. The cubic alum prepared by means of the alum-stone is preferred for its superior purity.

The purity of Roman alum is owing to the presence of the hydrate of aluminium in the alum-stone. This hydrate being in reality a much stronger base than ferric hydrate, when alum-stone is treated by water it enters into double decomposition with the iron salts contained in the liquor, hydrate of iron is precipitated, and the alum remains pure.

$$\underbrace{\left(\left.\begin{matrix}Fe^{2vi}\\(SO^{2''})^3\end{matrix}\right\}O^6,\ \left.\begin{matrix}SO^{2''}\\K^2\end{matrix}\right\}O^2 + 24\text{ aq.}\right)}_{\text{Iron alum.}} + \underset{\text{Hydrate of aluminium.}}{\left(\left.\begin{matrix}Al^{2vi}\\H^6\end{matrix}\right\}O^6\right)} =$$

$$\underset{\text{Ferric hydrate.}}{\left(\left.\begin{matrix}Fe^2\\H^6\end{matrix}\right\}O^6\right)} + \underbrace{\left(\left.\begin{matrix}Al^{2vi}\\(SO^{2''})^3\end{matrix}\right\}O^6,\ \left.\begin{matrix}SO^{2''}\\K^2\end{matrix}\right\}O^2 + 24\text{ aq.}\right)}_{\text{Ordinary alum.}}$$

The crystallization in cubes is owing to a small quantity of subsulphate of aluminium being present. If a solution of cubic alum be boiled for a long time it will deposit a small quantity of subsulphate of aluminium, and when filtered it leaves octahedral crystals.

Knowing the causes which make the Roman alum the purer, and determine its crystalline form, it is easy to purify artificial alum and to obtain it in the form desired by consumers. For this purpose a small quantity of carbonate of potassium is added to a solution of alum saturated at 45°; a little hydrate of aluminium is precipitated. This hydrate decomposes the iron salts contained in the solution, and besides gives rise to a little subsulphate of aluminium, so that the solution on cooling leaves alum as pure as the Roman alum, and, like it, crystallized in cubes.

However, cubic alum does not always contain the subsulphate of aluminium. M. Lowel has found that such crystals may be entirely free from this basic salt. According to him, the cubic form would be owing to the catalytic action exercised by the basic salt at the time of the crystallization.

Alum is strongly astringent; it is much more soluble in boiling than in cold water. When heated it undergoes aqueous fusion, and if then cooled it assumes a vitreous aspect, and constitutes what is called rock alum. If, on the contrary, the heat be continued, the water evaporates, the mass swells up, and a white matter is obtained, which rises above the crucible in which the calcination is made. This is the burnt alum of pharmacy—alum deprived of its 24 molecules of water of crystallization. This alum has an astringent taste and is slightly caustic; it is used as such in medicine.

When heated to a still higher temperature, the alum decomposes, the two sulphates of which it is formed are separated, the sulphate of potassium remains unaltered, and the sulphate of aluminium is destroyed, losing the elements of sulphuric anhydride; after the calcination the matter therefore consists of a mixture of alumina and sulphate of potassium.

Alums may be obtained in which the potassium is replaced by other alkaline metals; they are all isomorphous. That which contains ammonium, as its alkaline salt is decomposed by heat, leaves pure alumina when calcined.

**Silicate of Aluminium.**—This salt in a pure state constitutes kaolin, which is used in the manufacture of porcelain; when mixed with ferric silicate, it forms the clays of which the common potteries are manufactured. The silicate of aluminium is formed by lixiviating felspar rocks, which are really double silicates of aluminium and an alkaline metal. Water passing over these rocks for a length of time disintegrates them, seizing the alkaline silicate and leaving a residue of kaolin or China clay.

**Distinctive Characters of Salts of Aluminium.**—The salts of aluminium may be recognized by the following properties:

1st. They are precipitated by ammonia and the fixed alkalies. The precipitate dissolves in caustic potash or soda. Heat assists the solution.

2nd. Those salts are not precipitated by hydrosulphuric acid, but in presence of alkaline sulphides they give a precipitate of hydrate of aluminium.

3rd. Alkaline carbonates and the ammonic carbonate produce a precipitate that is insoluble in an excess of the reagent.

4th. If a hot concentrated solution of sulphate of potassium be added to an equally hot and concentrated solution of sulphate of aluminium, octahedral crystals of alum separate on cooling.

## MANGANESE Mn.

Atomic weight = 57. Molecular weight unknown.

Metallic manganese is obtained by calcining its oxides with charcoal, a carbide of manganese is thus produced which, when melted with a little carbonate of manganese, gives the pure metal. This metal is so brittle that it can be reduced to powder by trituration. Its density is 8·013; it is almost infusible. At 100° it easily decomposes water; in moist air it oxidizes so easily that it ought to be preserved in naphtha or in hermetically-sealed tubes.

The quantities of manganese which enter into combination are equal sometimes to one atom, sometimes to two. The compounds only containing one atom are called proto-compounds, those containing two, per-compounds (manganous and manganic compounds). Sub-compounds are seldom saturated; manganese acts in them as bivalent. The tetratomicity of this metal is seldom apparent except in the per compounds; two atoms united then form an hexatomic group, which could not occur unless each atom be allowed a maximum capacity for saturation equal to 4 at least.

Nevertheless, M. Nicklès has recently shown that manganese forms a chloride corresponding to the formula $(Mn^{iv}Cl^4)$. This chloride has not yet been isolated owing to its great instability, it decomposes into bichloride and chlorine.

$$\underset{\text{Tetrachloride of manganese.}}{\left(MnCl^4\right)} = \underset{\text{Bichloride of manganese.}}{\left(MnCl^2\right)} + \underset{\text{Chlorine.}}{\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}}$$

M. Nicklès rendered it stable by combining it with ethers. This chloride is formed, to be destroyed immediately, when the binoxide of manganese is treated by hydrochloric acid.

$$\underset{\text{Binoxide of manganese.}}{\left(MnO^2\right)} + \underset{\text{Hydrochloric acid.}}{4\left(\begin{matrix}H\\Cl\end{matrix}\right\}\Big)} = \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Tetrachloride of manganese.}}{\left(MnCl^4\right)}$$

The existence of the tetrachloride of manganese places the tetratomicity of this metal beyond doubt.

The compounds of manganese with monatomic radicles therefore answer either to the formula $(MnR'^2)$ or to $(Mn^2R'^6)$, or more rarely to $(Mn^{iv}R'^4)$.

Biatomic radicles also combine with manganese: the compounds answer to the general formula $(MnR'')$ when they are sub-compounds, and to $(Mn^2R''^3)$ when they are per-compounds; moreover, in consequence of the property biatomic radicles have of accumulating in indefinite numbers in molecules, these radicles may combine with manganese in much larger proportions than the two in question; thus four oxides of manganese are known:

The protoxide $(MnO)$, the sesquioxide $(Mn^2O^3)$, the red oxide $(Mn^3O^4)$, and the binoxide $(MnO^2)$.

Besides these, two kinds of salts are known: the manganates $(MnR'^2O^4)$ and the permanganates $(MnR'O^4)$. The anhydride corresponding to manganic acid would be $(MnO^3)$, and that corresponding to the permanganic acid would be $(Mn^2O^7)$. These two anhydrides are unknown, as is also the manganic acid $(MnH^2O^4)$, but the permanganic acid $(MnHO^4)$ has been obtained dissolved in water and appears also to exist in a solid state.

The *protoxide* is a basic anhydride soluble in acids forming salts. It is obtained by transmitting a current of dry hydrogen over gently-heated binoxide. In order to effect this, the binoxide is generally placed in a tube heated by a spirit-lamp. Thus prepared it can be preserved in air.

The hydrate of manganese may be obtained by precipitating a soluble manganous salt by an alkali: exposed to the air this becomes a per-hydrate.

The *anhydrous sesquioxide* is prepared by gently calcining the nitrate of manganese. It is a feeble basic anhydride. Dissolved in acids, it gives red per-salts which are very instable; but the sulphate acquires stability in presence of alkaline sulphates, with which it combines, giving salts which crystallize in the cubic system with 24 molecules of water. The double salt obtained with the sulphate of potassium ought to have for formula $\left(\left.\begin{matrix}(Mn^2)^{vi}\\(SO^{2''})^3\end{matrix}\right\}O^6,\ \left.\begin{matrix}SO^{2''}\\K^2\end{matrix}\right\}O^2 + 24\,aq.\right)$.

These salts are isomorphous with alums, and have for this reason received the name of manganic alums.

The *red oxide* may be written $\left(\left.\begin{matrix}(Mn^2)^{vi}\\Mn''\end{matrix}\right\}O^4\right)$. This compound may therefore be considered as a mixture of the protoxide and sesquioxide.

The *binoxide* $(MnO^2)$ exists native; it is the ore of manganese. Boiled in hydrochloric acid, it gives water and tetrachloride of manganese. This latter is destroyed as soon as formed, disengaging chlorine, and protochloride is formed, which is dissolved. If the solution of this chloride be submitted to the action of an alkaline carbonate it will give a precipitate of carbonate of manganese, by means of which all the sub-salts of this metal may be prepared.

The *manganate of potassium* $(MnK^2O^4)$ is obtained when a mixture of binoxide of manganese and potash is heated in contact with air, or, what is better, when the binoxide of manganese is calcined with a substance that is capable of yielding potassium and oxygen, like the nitrate of potassium.

The manganate of potassium is green; alkaline water dissolves it without alteration, but pure water, or water with a little nitric acid added, transforms this salt into a mixture of hydrated peroxide of manganese and permanganate of potassium:

$$\underset{\substack{\text{Manganate of}\\ \text{potassium.}}}{3\left(\mathrm{MnK^2O^4}\right)} + \underset{\text{Water.}}{2\left(\mathrm{H^2O}\right)} = \underset{\substack{\text{Binoxide}\\ \text{of manganese.}}}{\left(\mathrm{MnO^2}\right)} + \underset{\substack{\text{Permanganate}\\ \text{of potassium.}}}{2\left(\mathrm{MnKO^4}\right)} + \underset{\text{Potash.}}{4\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}$$

When a solution of potassic manganate is exposed to the air, the carbonic anhydride slowly produces the reaction just indicated, and as the colours of the manganate and permanganate of potassium are very different, a variety of shades are produced which caused this body to be formerly called mineral chameleon.

The *permanganate of potassium* is obtained by the calcination of a mixture of peroxide of manganese, hydrate of potassium, and chlorate of potassium. On dissolving in water, filtering through asbestos and evaporating in a porcelain capsule, crystals of permanganate of potassium are at once observed which answer to the formula $(\mathrm{MnKO^4})$.

The permanganate of potassium, added to solutions of the salts of the different metals, gives precipitates. The permanganate of barium, thus prepared by double decomposition, leaves the permanganic acid when treated by dilute sulphuric acid:

$$\underset{\substack{\text{Permanganate}\\ \text{of barium.}}}{\left((\mathrm{MnO^4})^2\mathrm{Ba}''\right)} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{\left(\mathrm{SO^{4}}''\mathrm{H^2}\right)} = \underset{\substack{\text{Sulphate}\\ \text{of barium.}}}{\left(\mathrm{SO^{4}}''\mathrm{Ba}''\right)} + \underset{\substack{\text{Permanganic}\\ \text{acid.}}}{2\left(\mathrm{MnO^4H}\right)}$$

Under the influence of potash, the permanganates are transformed into manganates:

$$\underset{\substack{\text{Permanganate}\\ \text{of potassium.}}}{4\left(\mathrm{MnKO^4}\right)} + \underset{\text{Potash.}}{4\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\substack{\text{Manganate of}\\ \text{potassium.}}}{4\left(\mathrm{MnK^2O^4}\right)} + \underset{\text{Water.}}{2\left(\mathrm{H^2O}\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\}}$$

The permanganates of potassium, sodium, barium, strontium, and silver, are isomorphous with the perchlorates of the same metals.

Soluble permanganates assume a beautiful violet colour.

**Reactions of Salts of Manganese.**—The salts of manganese are recognized by the following characters:

1st. These salts are rose-coloured, and become white when dried.

2nd. Heated with potash on a sheet of platinum in the oxidizing flame of the blowpipe, they give the green alkaline manganate.

3rd. Boiled with a mixture of binoxide of lead and nitric acid, they give a violet solution due to the permanganic acid formed. This test is very delicate.

4th. In solutions of the salts of manganese, potash and soda produce a white precipitate which rapidly darkens on exposure to the air.

5th. The soluble alkaline sulphides cause the formation of a flesh-coloured precipitate of hydrated sulphide of manganese. This precipitate dissolves in cold dilute hydrochloric acid.

## IRON, Fe.

Atomic weight = 56. Molecular weight unknown.

The only iron ores worked contain oxides of this metal. These are usually mixed with foreign matters (earthy impurities), which are sometimes calcareous and sometimes siliceous.

Oxide of iron may be reduced either by the Catalan method or by means of blast furnaces.

In both methods the oxygen is removed from the metal by bringing the ore into contact with the oxide of carbon at a high temperature. The oxide of carbon is produced by the direct combustion of charcoal which is mixed with the oxide of iron. The difference between the two methods is as follows:

In the furnaces, the quantity of calcareous matter requisite to transform the silica into silicate of lime is added to the ore, in order that iron in the state of silicate—which cannot be reduced by the oxide of carbon—be not lost. The fusion of the silicate of calcium requires a much higher temperature than that at which the oxide of iron is reduced, and at this high temperature the iron unites with the charcoal, and gives cast or pig iron, which must be kept melted in a strong current of air in order to burn the carbon it contains, and to cause it to pass to the state of wrought iron.

In the Catalan method the temperature is not so high. Instead of the silicate of calcium, silicate of iron, which is much more fusible, is formed, and as the heat never attains the degree at which the charcoal combines with the iron, wrought iron is at once obtained instead of cast iron. This process has one great inconvenience, which is, that it causes one part of iron in the state of silicate to be lost, and consequently it is only employed for very rich ores.

We have said that cast iron is a combination of carbon and iron. There also exists a less carburetted combination of iron which is called steel, and which possesses the property of becoming very hard when tempered. It is prepared either by heating iron with charcoal (cemented steel) or by imperfectly burning the carbon from cast iron.

The first method produces steel of the best quality.

Lately, it has been stated that besides iron and carbon, steel also contains a certain quantity of nitrogen, but this opinion has been strongly contested.

The presence of certain foreign bodies, such as titanium, possesses the property of considerably hardening steel. For several years the titanic irons of Australia have been worked in England for the manufacture of steel.

The iron obtained by manufacturers always contains foreign substances. In order to procure the pure metal, absolutely pure sesquioxide of iron is prepared, and reduced by hydrogen. The metal must then be aggregated by heating, or else it is pyrophoric.

Iron possesses a crystalline texture; it is sometimes in brilliant grains and sometimes fibrous. The latter is preferred, as it has more tenacity than the other.

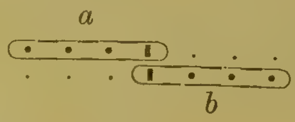
Iron is the most tenacious of all metals. It only melts at a very high temperature. At a white heat it is sufficiently soft to be welded, a property which is very important in manufactures.

Iron is not altered either by oxygen or dry air. In moist air it oxidizes and becomes covered with rust; the presence of carbonic anhydride facilitates this. The oxidation takes place at the cost of the water, and the nascent hydrogen unites with the nitrogen of the air, forming ammonia, with which the rust is always impregnated.

Iron decomposes water at red heat, liberating hydrogen. At this temperature it also unites directly with the oxygen of the atmosphere. Such an oxide constitutes the pieces that are detached from the hot metal when it is hammered. When cold, iron dissolves in acids, disengaging hydrogen.

With monatomic radicles iron forms two series of compounds: in the first, a single atom of this metal intervenes, which in this case is never saturated, and though tetratomic, it acts as bivalent. To these compounds correspond others of the same order, which are formed by the union of iron with biatomic radicles. All these compounds are sub- or ferrous compounds.

Iron also forms combinations which do not contain a single atom of this metal, but the group $Fe^2$. This group is naturally hexatomic, because the two atoms of iron mutually exchange an atomicity, as is shown in the following figure:



in which *a* and *b* represent two atoms of tetratomic iron, giving rise to the group $Fe^2$, in which only six free centres of attraction are found instead of eight.

The group $Fe^2$ is therefore capable of uniting either with six monatomic or with three biatomic radicles. The compounds of this order are generally called per- or ferric compounds.

The principal per- and sub-compounds of iron are the following:

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| FERROUS OR PROTO-COMPOUNDS. | |
|---|---|
| Protochloride of iron . | $(FeCl^2)$ |
| Protobromide . . . | $(FeBr^2)$ |
| Prot-iodide . . . . | $(FeI^2)$ |
| Protofluoride . . . | $(FeFl^2)$ |
| Hydride . . . . . . | $(FeH^2)$ |
| Protoxide . . . . | $(FeO)$ |
| Protosulphide . . . | $(FeS)$ |
| Proto-salts. . . . . | $\left(\left.\begin{matrix}Fe\\(R')^2\end{matrix}\right\}O^2\right)$ |

| FERRIC OR PER-COMPOUNDS. | |
|---|---|
| Perchloride of iron . | $(Fe^2Cl^6)$ |
| Perbromide . . . . | $(Fe^2Br^6)$ |
| Periodide . . . . . | $(Fe^2I^6)$ |
| Perfluoride . . . . | $(Fe^2Fl^6)$ |
| Sesquioxide . . . . | $(Fe^2O^3)$ |
| Sesquisulphide . . . | $(Fe^2S^3)$ |
| Perhydrate of iron . | $\left(\left.\begin{matrix}Fe^2\\H^6\end{matrix}\right\}O^6\right)$ |
| Various per-salts . . | $\left(\left.\begin{matrix}Fe^2\\(R')^6\end{matrix}\right\}O^6\right)$ |

R′ being any monatomic acid radicle.

Owing to the property biatomic radicles possess of accumulating in molecules, oxygen and sulphur, in addition to the preceding compounds, form

| | |
|---|---|
| Magnetic oxide of iron . . . . . . | $(Fe^3O^4)$ |
| Ferric anhydride . . . . . . . | $(FeO^3)$ |
| Bisulphide of iron . . . . . . . | $(FeS^2)$ |
| Magnetic pyrites . . . . . . . | $(Fe^7S^8)$ |

## SUB-COMPOUNDS OF IRON.

**Protochloride of Iron** $(Fe''Cl^2)$.—Anhydrous protochloride of iron

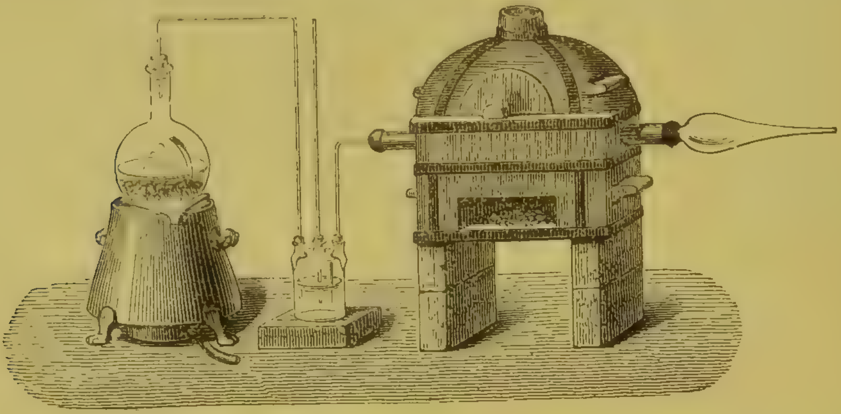


Fig. 36.

is obtained by directing a current of dry hydrochloric acid gas (fig. 36) through a porcelain tube containing pure iron heated to redness.

$$\underset{\text{Iron.}}{Fe} + \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}} + \underset{\text{Protochloride of iron.}}{\left(Fe''Cl^2\right)}$$

The salt condenses in brilliant scales on the sides of the cold part of the tube.

Ferrous chloride is volatile, soluble in water and in alcohol. Its aqueous solution is green, and when evaporated, deposits green hydrated crystals ($FeCl^2 + 4$ aq.) Exposed to the air, this solution absorbs oxygen, becomes turbid, and its colour yellow; in this case an oxychloride is formed.

$$4\underset{\text{Protochloride of iron.}}{\left(Fe''Cl^2\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} = 2\underset{\text{Oxychloride of iron.}}{\left(Fe^2Cl^4O\right)}$$

If an acid and an oxidizing body be caused to act simultaneously on the protochloride of iron, a double per-salt is formed.

$$4\underset{\text{Protochloride of iron.}}{\left(FeCl^2\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} + 4\underset{\text{Nitric acid.}}{\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)}$$

$$= 2\underset{\text{Tetrachloro-dinitrate of iron.}}{\left(Fe^{IV2}\left\{\begin{matrix}ONO^2\\ONO^2\\Cl^4\end{matrix}\right.\right)} + 2\underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

Chlorine combines with the ferrous chloride and transforms it into ferric chloride:

$$2\underset{\text{Ferrous chloride.}}{\left(Fe''Cl^2\right)} + \underset{\text{Chlorine.}}{\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}} = \underset{\text{Ferric chloride.}}{\left(Fe^2Cl^6\right)}$$

**Protobromide of Iron** ($FeBr^2$).—The properties and the mode of preparation of this body are similar to the preceding one, it is therefore unnecessary to describe it.

**Prot-iodide of Iron** ($FeI^2$).—The hydrated prot-iodide of iron is prepared for medicinal purposes by triturating 56 parts of iron with 254 parts of iodine in water: it is better to use a larger proportion of iron than 56 in order that the metal be in excess. When the liquid has lost all smell of iodine, it is filtered and rapidly evaporated. On cooling, green crystals of iodide of iron are left.

The contact of air must be avoided as much as possible during this process; the ferrous iodide quickly alters in air, absorbing oxygen and being converted into ferric oxyiodide.

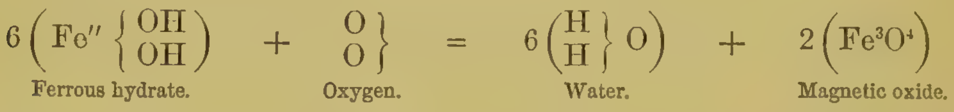
**Protoxide of Iron** ($FeO$).—When equal volumes of carbonic anhydride and oxide of carbon are transmitted over red-hot sesquioxide of iron, the iron is reduced to the state of protoxide. This body always contains a small quantity of the sesquioxide.

A hydrate of iron is obtained by precipitating a ferrous salt by potash:

$$\underset{\text{Protochloride of iron.}}{\left(Fe''Cl^2\right)} + 2\underset{\text{Potash.}}{\left(KOH\right)} = 2\underset{\text{Chloride of potassium.}}{\left(KCl\right)} + \underset{\text{Ferrous hydrate.}}{\left(Fe''\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)}$$

This hydrate is so unstable that it cannot be dehydrated without being destroyed.

Ferrous hydrate is green when precipitated, but it quickly becomes yellow and is transformed into magnetic oxide.

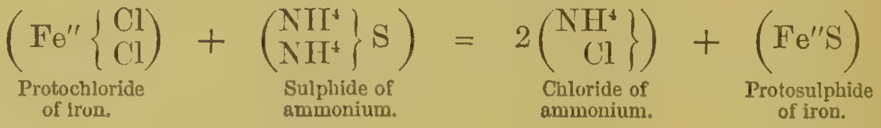


$$\underset{\text{Ferrous hydrate.}}{6\left(\mathrm{Fe''}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}\right.\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\}} = \underset{\text{Water.}}{6\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Magnetic oxide.}}{2\left(\mathrm{Fe^{3}O^{4}}\right)}$$

Hydrate of iron is a true base, capable of exchanging its hydroxyl for the halogen residue of acids.

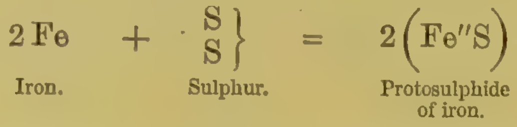
**Protosulphide of Iron** ($FeS$).—This body may be prepared either by precipitating a ferrous salt by the sulphide of ammonium or by heating a mixture in atomic proportions of sulphur and iron.

1st.



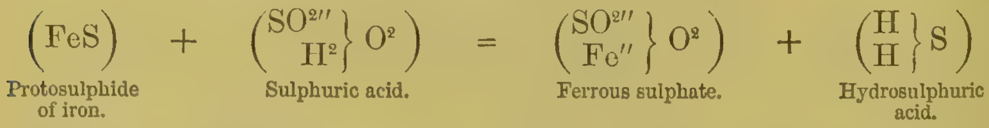
$$\underset{\text{Protochloride of iron.}}{\left(\mathrm{Fe''}\left\{\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right.\right)} + \underset{\text{Sulphide of ammonium.}}{\left(\left.\begin{matrix}\mathrm{NH^{4}}\\ \mathrm{NH^{4}}\end{matrix}\right\}\mathrm{S}\right)} = \underset{\text{Chloride of ammonium.}}{2\left(\left.\begin{matrix}\mathrm{NH^{4}}\\ \mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\text{Protosulphide of iron.}}{\left(\mathrm{Fe''S}\right)}$$

2nd.



$$\underset{\text{Iron.}}{2\,\mathrm{Fe}} + \underset{\text{Sulphur.}}{\left.\begin{matrix}\mathrm{S}\\ \mathrm{S}\end{matrix}\right\}} = \underset{\text{Protosulphide of iron.}}{2\left(\mathrm{Fe''S}\right)}$$

The sulphide prepared by the first method is pulverulent, black, and easily absorbs oxygen, passing to the state of sulphate. That obtained by the second method is hard, brittle, and possesses a metallic lustre. In either case the sulphide of iron is attacked by dilute acids, forming a ferrous salt, and disengaging hydrosulphuric acid:



$$\underset{\text{Protosulphide of iron.}}{\left(\mathrm{FeS}\right)} + \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}\mathrm{SO^{2\prime\prime}}\\ \mathrm{H^{2}}\end{matrix}\right\}\mathrm{O^{2}}\right)} = \underset{\text{Ferrous sulphate.}}{\left(\left.\begin{matrix}\mathrm{SO^{2\prime\prime}}\\ \mathrm{Fe''}\end{matrix}\right\}\mathrm{O^{2}}\right)} + \underset{\text{Hydrosulphuric acid.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{S}\right)}$$

A mixture of iron filings and flowers of sulphur moistened, react on each other at the end of a certain time; the reaction is accompanied by a great disengagement of heat. If the mixture be buried not very deeply, and if it be in considerable quantity, the vapour of water which forms projects the earth some distance, and sometimes even the combination is accompanied by disengagement of light. Lémery believed he could account for volcanic action in this manner, and the experiment is known as Lémery's volcano.

**Ferrous Sulphate** $\left(\left.\begin{matrix}\mathrm{SO^{2\prime\prime}}\\ \mathrm{Fe''}\end{matrix}\right\}\mathrm{O^{2}} + 7\ \mathrm{aq.}\right)$ (*Protosulphate*).—In the laboratory this salt is prepared by dissolving iron in dilute sulphuric acid, concentrating the liquid by boiling, and leaving it to cool for the salt to be deposited in crystals.

In the arts, this body is usually prepared by roasting native pyrites (bisulphide of iron).

$$\underset{\text{Pyrites.}}{\left(FeS^2\right)} + \underset{\text{Oxygen.}}{3\left(\left\{\begin{matrix}O\\O\end{matrix}\right\}\right)} = \underset{\text{Sulphurous anhydride.}}{\left(SO^2\right)} + \underset{\text{Ferrous sulphate.}}{\left(SFeO^4\right)}$$

After roasting it is washed, the liquor left to clear, then decanted, suitably evaporated, and the salt is crystallized.

Certain pyrites absorb oxygen by simple exposure to the air without it being necessary to heat them.

The sulphate of iron thus prepared contains many impurities, among which is copper. This is eliminated by placing sheets of iron for some time in the solution of the sulphate: the iron is substituted for the copper which precipitates.

Sulphate of iron is known in commerce as green vitriol or green copperas.

Ferrous sulphate crystallizes in greenish oblique rhomboidal prisms, which contain seven molecules of water. It has an astringent taste. One part of this salt requires for its solution 1·42 of water at 15°, and 0·33 of boiling water. It is insoluble in alcohol, but this liquid takes from it six molecules of water; it also loses six-sevenths of its water of crystallization when heated to 100°, but it only becomes entirely anhydrous at 300°.

When calcined, the ferrous sulphate decomposes into sulphurous anhydride, sesquioxide of iron, and sulphuric anhydride: it will be remembered that the preparation of Nordhausen sulphuric acid is founded on this reaction.

$$\underset{\text{Ferrous sulphate.}}{2\left(\left.\begin{matrix}SO^{2''}\\Fe''\end{matrix}\right\} O^2\right)} = \underset{\text{Sulphurous anhydride.}}{\left(SO^2\right)} + \underset{\text{Sulphuric anhydride.}}{\left(SO^3\right)} + \underset{\text{Sesquioxide of iron.}}{\left(Fe^2O^3\right)}$$

Exposed to air, the crystals or the solution of the ferrous sulphate absorb oxygen, and give a yellowish ferric subsulphate, which may be decomposed by boiling it with iron.

The protosulphate of iron in aqueous solution can only be preserved by the water in which it is dissolved being previously deprived of air by boiling, and the solution being carefully preserved from contact with air.

Sulphate of iron when crystallized with seven molecules of water is isomorphous with the sulphates of the magnesian series.

## PER-COMPOUNDS OF IRON.

**Perchloride of Iron** ($Fe^2Cl^6$).—The anhydrous perchloride of iron is obtained by transmitting an excess of chlorine over red-hot iron, in the apparatus used to prepare the ferrous chloride.

It may also be prepared by distilling at red heat in an earthen retort, hydrated perchloride prepared by the solution of iron in aqua regia. In the latter case, however, one part of the perchloride is decomposed by water into hydrochloric acid and sesquioxide of iron.

$$\underset{\text{Perchloride of iron.}}{\left(Fe^2Cl^6\right)} + 3\underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = 6\underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Sesquioxide of iron.}}{\left(Fe^2O^3\right)}$$

Hydrated perchloride of iron may also be procured by dissolving per-hydrate of iron in hydrochloric acid.

$$\underset{\text{Ferric hydrate.}}{\left(\left.\begin{matrix}Fe^{2vi}\\H^6\end{matrix}\right\}O^6\right)} + 6\underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\text{Ferric chloride.}}{\left(Fe^2Cl^6\right)} + 6\underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

On evaporating the solution and allowing it to cool, rhombohedral laminæ of a beautiful yellow colour are obtained, which answer to the formula ($Fe^2Cl^6 + 6$ aq).

Anhydrous ferric chloride is the colour of the wings of the Spanish fly. It is volatile: water, alcohol and ether dissolve it; water causing it to pass to the state of hydrated chloride. Submitted to the action of the vapour of water in a heated tube, this body gives crystallized sesquioxide of iron, which is identical with the specular iron found native.

Ferric chloride in aqueous solution is employed in medicine both externally and internally as a hæmostatic, on account of the property it possesses of coagulating albumen.

**Perbromide and Periodide of Iron.**—These bodies may be obtained by combining directly iron with bromine or iodine in excess. They are not used.

**Sesquioxide of Iron** ($Fe^2O^3$).—In commerce this body (colcothar) is prepared by calcining ferrous sulphate; in the laboratory it is prepared in preference by heating ferric hydrate.

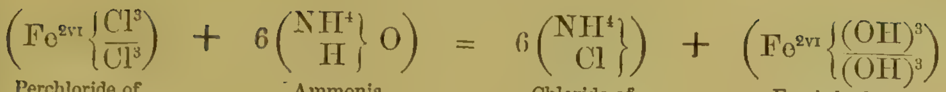
In nature this body is found crystallized; it is then isomorphous with alumina.

The sesquioxide of iron is a basic anhydride. Nevertheless, weak acids do not dissolve it; only strong and boiling acids attack it, transforming it into ferric salts.

When finely-powdered sesquioxide of iron is heated in a current of dry hydrogen, the oxide is entirely reduced, and iron in an extreme state of division is obtained. This iron is pyrophoric, unless it be aggregated by heat at the end of the operation.

**Ferric Hydrate** $\left(\left.\begin{matrix}Fe^{2vi}\\H^6\end{matrix}\right\}O^6\right)$.—A basic hydrate corresponds to the sesquioxide of iron, the ferric hydrate, which is generally prepared by the decomposition of a soluble ferric compound by means of ammonia.

The precipitate which forms must be collected on a filter, and well washed.



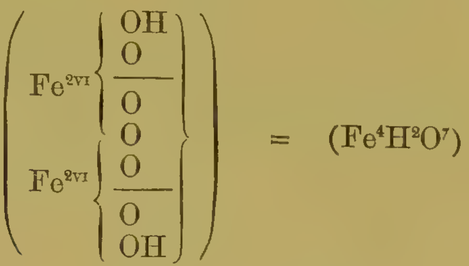
$$\left(\mathrm{Fe}^{2vi}\left\{\begin{matrix}\mathrm{Cl}^3\\ \hline \mathrm{Cl}^3\end{matrix}\right.\right) + 6\left(\left.\begin{matrix}\mathrm{NH}^4\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right) = 6\left(\left.\begin{matrix}\mathrm{NH}^4\\ \mathrm{Cl}\end{matrix}\right\}\right) + \left(\mathrm{Fe}^{2vi}\left\{\begin{matrix}(\mathrm{OH})^3\\ \hline (\mathrm{OH})^3\end{matrix}\right.\right)$$

Perchloride of iron. Ammonia. Chloride of ammonium. Ferric hydrate.

Ferric hydrate is still more easily reducible by hydrogen than is colcothar. The most feeble acids dissolve it, giving rise to per-salts.

When calcined, it loses its water and becomes anhydrous. At the instant this transformation takes place, the mass becomes incandescent. Suspended in a concentrated alkaline solution through which a current of chlorine is directed, the ferric hydrate rapidly passes to the state of alkaline ferrate.

According to M. Péan de Saint-Gilles, when the ferric hydrate is boiled for seven or eight hours, it loses a great quantity of water, and is converted into a condensed anhydride, the formula of which is:



$$\left(\begin{matrix}\mathrm{Fe}^{2vi}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{O}\\ \hline \mathrm{O}\end{matrix}\right.\\ \mathrm{O}\\ \mathrm{Fe}^{2vi}\left\{\begin{matrix}\mathrm{O}\\ \hline \mathrm{O}\\ \mathrm{OH}\end{matrix}\right.\end{matrix}\right) = (\mathrm{Fe}^4\mathrm{H}^2\mathrm{O}^7)$$

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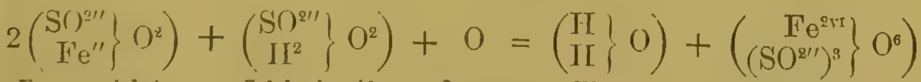
This new compound no longer presents the phenomena of incandescence when calcined, and is dissolved with as much difficulty in acids as the anhydrous sesquioxide.

Mr. Graham has obtained a soluble variety of ferric hydrate by submitting the ferric acetate to dialysis. This soluble hydrate appears to be a condensed compound.

**Per-Salts of Iron.**—These are obtained by dissolving the ferric hydrate in different acids. They may also be prepared by dissolving ferrous salts in water and peroxidizing them by a current of chlorine or by nitric acid. In the latter case, if we wish to obtain a neutral salt, a certain quantity of the acid, the elements of which are contained in the salt, must be added to the solution. With an equal quantity of metal per-salts always contain a greater number of molecules of the electro-negative group than the sub-salts, because in the latter the atom of iron is only bivalent, while in the former the double atom $\mathrm{Fe}^2$ is hexavalent.

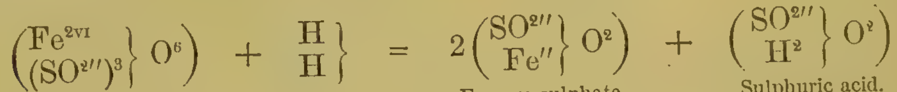
The following equation clearly shows the necessity of adding an acid to the ferrous salt which is to be peroxidized.



$$2\left(\left.\begin{matrix}\mathrm{SO}^{2''}\\ \mathrm{Fe}''\end{matrix}\right\}\mathrm{O}^2\right) + \left(\left.\begin{matrix}\mathrm{SO}^{2''}\\ \mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right) + \mathrm{O} = \left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right) + \left(\left.\begin{matrix}\mathrm{Fe}^{2vi}\\ (\mathrm{SO}^{2''})^3\end{matrix}\right\}\mathrm{O}^6\right)$$

Ferrous sulphate. Sulphuric acid. Oxygen. Water. Neutral ferric sulphate.

When a reducing agent is made to act on ferric salts, they are transformed into ferrous salts, and at the same time one molecule of acid becomes free.



$$\left(\left.\begin{matrix}\mathrm{Fe}^{2\mathrm{vi}}\\(\mathrm{SO}^{2''})^3\end{matrix}\right\}\mathrm{O}^6\right) + \left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\} = 2\left(\left.\begin{matrix}\mathrm{SO}^{2''}\\\mathrm{Fe}''\end{matrix}\right\}\mathrm{O}^2\right) + \left(\left.\begin{matrix}\mathrm{SO}^{2''}\\\mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right)$$

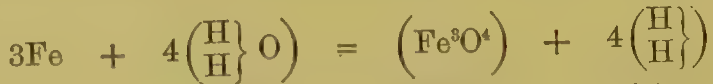
Ferric sulphate. Hydrogen. Ferrous sulphate. Sulphuric acid.

The reducing agents which can produce this result are, among others, hydrosulphuric acid, nascent hydrogen, and iron filings. In the case of hydrosulphuric acid, the reduction takes place without heat being required, sulphur is deposited, and sulphuric acid is liberated; in that of iron filings, on the contrary, the solution of the salt to be reduced must be boiled with this body; then instead of free sulphuric acid ferrous sulphate is formed.

## COMPOUNDS OF IRON WHICH DO NOT BELONG TO EITHER OF THE TWO PRECEDING SERIES.

**Magnetic Oxide of Iron** ($Fe^3O^4$).—This oxide is found native, and constitutes an excellent iron ore. Natural loadstones are composed of it.

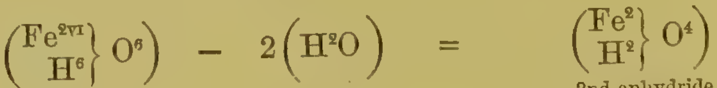
It may be produced artificially by passing vapour of water over red-hot iron.



$$3\mathrm{Fe} + 4\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right) = \left(\mathrm{Fe}^3\mathrm{O}^4\right) + 4\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\right)$$

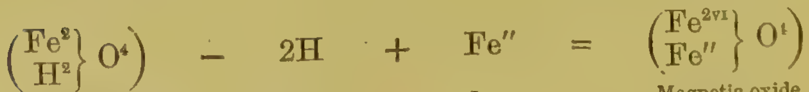
Iron. Water. Magnetic oxide of iron. Hydrogen.

It may also be prepared by precipitating by ammonia a mixture of protochloride and perchloride of iron, containing quantities of each of these bodies corresponding to the weights of their molecules. In this case it is necesssary to pour the mixture drop by drop into a great excess of ammonia. If, on the contrary, ammonia were poured into the mixture, the alkali not being everywhere in excess, ferric hydrate would first precipitate, then ferrous hydrate, and no magnetic oxide. The magnetic oxide ought to be regarded as a sub-salt of iron formed by the second anhydride of the per-hydrate of the metal acting as an acid.



$$\left(\left.\begin{matrix}\mathrm{Fe}^{2\mathrm{vi}}\\\mathrm{H}^6\end{matrix}\right\}\mathrm{O}^6\right) - 2\left(\mathrm{H}^2\mathrm{O}\right) = \left(\left.\begin{matrix}\mathrm{Fe}^2\\\mathrm{H}^2\end{matrix}\right\}\mathrm{O}^4\right)$$

Ferric hydrate. Water. 2nd anhydride of the perhydrate of iron.



$$\left(\left.\begin{matrix}\mathrm{Fe}^2\\\mathrm{H}^2\end{matrix}\right\}\mathrm{O}^4\right) - 2\mathrm{H} + \mathrm{Fe}'' = \left(\left.\begin{matrix}\mathrm{Fe}^{2\mathrm{vi}}\\\mathrm{Fe}''\end{matrix}\right\}\mathrm{O}^4\right)$$

2nd anhydride of the perhydrate of iron. Hydrogen. Iron. Magnetic oxide of iron.

There exist, in fact, aluminates of iron isomorphous with it, which leaves no doubt as to its true constitution.

**Ferric Anhydride** ($FeO^3$).—Ferric anhydride is not known, but when a current of chlorine is directed through a concentrated alkaline solution holding ferric hydrate in suspension, a red salt is formed, which is the ferrate of potassium ($FeK^2O^4$), corresponding to the manganate of potassium ($MnK^2O^4$).

**Bisulphide of Iron** ($FeS^2$) (*Pyrites*).—Pyrites represents a saturated per-compound of iron. It is the only one known, and exists native, crystallized sometimes in cubes, sometimes in prisms. Cubic pyrites is the most common; it is so hard that it can cut glass, and strikes fire with steel. Its density varies from 4·083 to 5·031 according to Dana, and from 5·0 to 5·2 according to Rammelsberg. It has a metallic appearance. Simple acids do not affect it, but aqua regia easily attacks it. Sometimes this pyrites oxidizes in air, and sometimes it cannot be oxidized. The prismatic pyrites always oxidizes with ease. Heated with charcoal, the bisulphide of iron gives sulphide of carbon and protosulphide of iron.

**Magnetic Pyrites** ($Fe^7S^8$).—This body is found native, crystallized in regular hexahedral prisms. It acts as a magnet, and is of a bronze colour. It has not a very constant composition, appearing to result from the combination of various sulphides among themselves, without its being exactly known what are the sulphides thus combined.

It may be obtained artificially by heating a piece of iron to white heat, and then plunging it into a crucible full of melted sulphur: the pyrites falls to the bottom of the crucible.

**Titanic Iron.**—There exists in nature a body called titanic iron, which contains iron, titanium, and oxygen. This body is isomorphous with natural sesquioxide of iron. To explain this isomorphism, the titanic iron must be considered as a mixture of sesquioxide of iron ($Fe^2O^3$) and of an oxide ($TiFeO^3$), which is the same, except that an atom of iron is replaced by an atom of titanium. If this interpretation be correct, the substitution of an atom of tetratomic titanium for an atom of iron, and the isomorphism of this product of substitution with the ordinary oxide of iron, furnish another proof in favour of the tetratomicity of iron.

**Characters of the Salts of Iron.**—Proto-salts are generally green, and per-salts yellow, they are distinguished by the following characters:

1st. The ferrocyanide of potassium (yellow prussiate of potash) precipitates per-salts of iron blue, and proto-salts white.

2nd. The ferricyanide of potassium (red prussiate of potash) precipitates proto-salts of iron blue and does not precipitate per-salts.

3rd. With proto-salts the alkalies give a green precipitate which turns yellow in the air, and with per-salts a reddish precipitate which does not alter.

4th. Hydrosulphuric acid does not act on proto-salts, but reduces per-salts, depositing sulphur.

5th. With both classes of these salts the alkaline sulphides give a black precipitate which is very soluble in dilute acids.

## CHROMIUM Cr.

Atomic weight = 53·5. Molecular weight unknown.

Chromium may be extracted from its sesquioxide by means of charcoal at the temperature of a strong forge fire. The product always contains charcoal, from which it is freed by a second fusion in presence of the sesquioxide of chromium and borax.

Chomium may also be obtained by heating the perchloride of this metal with sodium, and then removing by water the chloride of sodium formed.

According to M. Wœhler, chromium may be obtained by reducing its perchloride by zinc.

Prepared by the first process, chromium has a metallic aspect. It is hard and brittle; its density is equal to 6·0; it becomes magnetic at 15° or 20°, but is not so at the ordinary temperature.

At red heat chromium absorbs oxygen, and passes to the state of sesquioxide. The acids, and even aqua regia scarcely affect it, but in presence of alkalies and of an oxidizing body like chlorate or nitrate of potassium, it passes to the state of alkaline chromate.

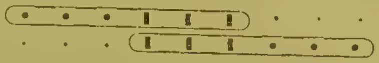
Chromium combines with chlorine, forming two chlorides which correspond to the two chlorides of iron. These are:

| | |
|---|---|
| The protochloride . . . . . . | $CrCl^2$. |
| And the perchloride . . . . . | $Cr^2Cl^6$. |

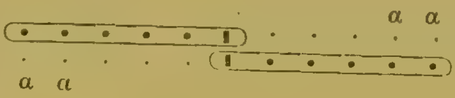
It has been stated that there also exists a chloride of chromium corresponding to the formula $CrCl^4$; also a bromide, an iodide, and a fluoride, the formulas of which would be $CrR^6$, R representing bromine or one of its congeners. However, these compounds are so unstable that up to the present time they have not been isolated in a free state, with the exception of the fluoride. Unfortunately, this body corrodes glass, which renders its analysis and the study of its properties very difficult.

The true formula of these different compounds of chromium is not therefore fixed as yet. It appears nevertheless certain, that they contain at least four, and perhaps six atoms of the monatomic metalloid for one of the metal.

This supports our views of the atomicity of chromium, which we consider as being more than two. It is true that we remain in doubt about this atomicity, and that we hesitate between the Nos. 4 and 6. If it were demonstrated that chromium is hexatomic, iron, manganese, aluminium, nickel, and cobalt must also be hexatomic, though they are never seen to act with an atomicity greater than 4. Nevertheless, as the tetratomicity of these different metals rests, not on the existence of the slightly known compounds of chromium of which we have just been speaking, but on other important considerations which have been previously developed, I have thought it right to regard them as tetratomic, reserving the admission of their hexatomicity if ever the formula ($CrFl^6$) of the fluoride of chromium be verified. It must be remarked that if iron, aluminium, etc., were hexatomic, the groups formed by the union of two atoms of these metals might, nevertheless, only be hexatomic. It would suffice for this that the two atoms which constitute them should exchange six atomicities instead of two, as the following figure indicates:



However, as this hypothesis does not account for the substitution of titanium for iron in titanic iron, I should prefer to admit that these atoms only exchange two affinities; and if the group be only hexatomic in appearance, it is simply because each atom has two centres of attraction, which in ordinary cases do not act, as the following figure, in which the inactive centres of attraction are designated by the letter *a*, shows.



These hypotheses need not be taken into consideration until the formula ($CrFl^6$) of the perfluoride of chromium is surely established; until then we must hold to the tetratomicity of chromium and of its congeners, iron, manganese, aluminium, cobalt, and nickel.

With oxygen chromium forms a series of compounds, which is as complete as the series of oxides of manganese, and more so than that of iron. In order to show these relations, we will write these three series as they stand in regard to each other:

| | Chromium series. | Manganese series. | Iron series. |
|---|---|---|---|
| Protoxide . . . . . . | $CrO$ | $MnO$ | $FeO$ |
| Saline oxide . . . . . | $Cr^3O^4$ | $Mn^3O^4$ | $Fe^3O^4$ |
| Sesquioxide . . . . . | $Cr^2O^3$ | $Mn^2O^3$ | $Fe^2O^3$ |
| Binoxide . . . . . . | $CrO^2$ | $MnO^2$ | wanting |
| Anhydride . . . . . . | $CrO^3$ | $MnO^3$ | $FeO^3$ |
| Per-anhydride . . . . . | $Cr^2O^7$ | $Mn^2O^7$ | wanting |

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The manganic, permanganic, and ferric anhydrides appear here only because the acids or salts derived from them are known. The bodies themselves are not known in the isolated state.

## Haloid Compounds of Chromium.

**Protochloride of Chromium** ($CrCl^2$).—The protochloride of chromium is prepared by causing hydrogen to act on the perchloride heated to redness:

$$\underset{\text{Perchloride of chromium.}}{\left(Cr^2\left\{\frac{Cl^3}{Cl^3}\right.\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}} = \underset{\text{Protochloride of chromium.}}{2\left(CrCl^2\right)} + \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)}$$

This body is white, crystalline, and soluble in water. In air its aqueous solution absorbs oxygen and gives an oxychloride ($Cr^2Cl^4O$).

**Perchloride of Chromium** $\left(Cr^2\left\{\frac{Cl^3}{Cl^3}\right.\right)$.—Both hydrated and anhydrous perchloride of chromium may be obtained. The hydrated is prepared by dissolving the basic hydrate $\left(\left.\begin{matrix}Cr^{2vi}\\H^6\end{matrix}\right\}O^6\right)$ in hydrochloric acid.

$$\underset{\text{Perhydrate of chromium.}}{\left(\left.\begin{matrix}Cr^{2vi}\\H^6\end{matrix}\right\}O^6\right)} + \underset{\text{Hydrochloric acid.}}{6\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\text{Water.}}{6\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Perchloride of chromium.}}{\left(Cr^2\left\{\frac{Cl^3}{Cl^3}\right.\right)}$$

It then assumes a green colour and is extremely soluble in water. When treated with nitrate of silver it only loses one-third of its chlorine at first, but if the solution be boiled the chlorine is entirely precipitated.

Anhydrous perchloride may be obtained by a method analogous to that used in the preparation of the perchloride of aluminium. An intimate mixture is made of sesquioxide of chromium and powdered charcoal; the mixture is kneaded with starch, and the paste thus formed is made into pellets and calcined. Thus, small porous masses are formed of the sesquioxide of chromium and charcoal, the starch becoming carbonized by calcination.

These balls are placed in an earthenware tube heated to redness, and submitted to the action of a current of dry chlorine. Carbonic anhydride is produced, which is disengaged, and perchloride of chromium, which is deposited in the cold part of the tube.

$$\underset{\text{Sesquioxide of chromium.}}{\left(Cr^2O^3\right)} + \underset{\text{Carbon.}}{3C} + \underset{\text{Chlorine.}}{3\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}\right)} = \underset{\text{Oxide of carbon.}}{3\left(CO\right)} + \underset{\text{Perchloride of chromium.}}{\left(Cr^2\left\{\frac{Cl^3}{Cl^3}\right.\right)}$$

Anhydrous perchloride of chromium is presented in the form of crystalline scales, whose colour resembles peach blossom. It is quite insoluble in pure water, but if the water contain only $\frac{1}{10000}$ of protochloride of chromium it will then dissolve and become hydrated. This curious fact has been accounted for by supposing that the protochloride takes the chlorine from a part of the perchloride and passes to the state of hydrated perchloride. The protochloride, formed at the cost of the reduced perchloride, would act in the same way on a new quantity of this latter body, and so on, so that the mass would be gradually wholly reduced first into protochloride and then into the state of soluble hydrated perchloride.

## COMBINATIONS OF CHROMIUM WITH BIATOMIC METALLOIDS.

**Protoxide of Chromium** ($CrO$).—This body possesses no interest. It is excessively unstable, and cannot be prepared pure. Its corresponding hydrate is obtained by precipitating the protochloride of chromium by alkalies.

$$\underset{\text{Protochloride of chromium.}}{\left(CrCl^2\right)} + \underset{\text{Potash.}}{2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Chloride of potassium.}}{2\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)} + \underset{\text{Hydrate of chromium.}}{\left(\left.\begin{matrix}Cr''\\H^2\end{matrix}\right\}O^2\right)}$$

**Sesquioxide of Chromium** ($Cr^2O^3$).—The sesquioxide may be obtained by a great number of different processes, the most simple of which appears to consist in calcining mercurous chromate in an earthen crucible. The mercury and a part of the oxygen contained in this salt are disengaged, and there remains sesquioxide of chromium.

$$\underset{\text{Mercurous chromate.}}{4\left(\left.\begin{matrix}CrO^{2''}\\Hg^{2''}\end{matrix}\right\}O^2\right)} = \underset{\text{Mercury.}}{8Hg} + \underset{\text{Oxygen.}}{5\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\right)} + \underset{\text{Sesquioxide of chromium.}}{2\left(Cr^2O^3\right)}$$

In order to obtain this body crystallized, it must be prepared by transmitting a current of chloride of chromyl in vapour through a porcelain tube heated to redness.

$$\underset{\text{Chloride of chromyl.}}{4\left(CrO^2Cl^2\right)} = \underset{\text{Sesquioxide of chromium.}}{2\left(Cr^2O^3\right)} + \underset{\text{Chlorine.}}{4\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}}$$

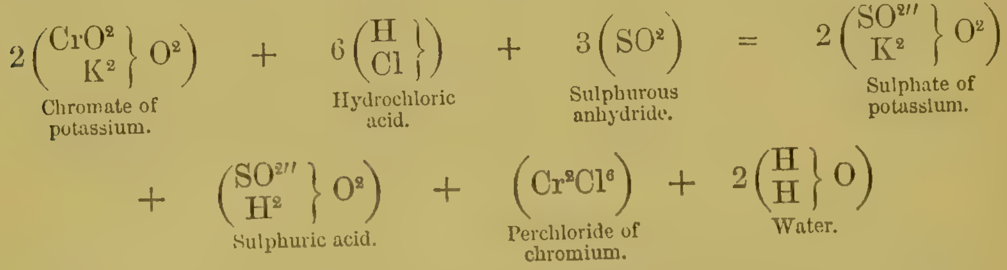
The crystals of sesquioxide of chromium have the form of rhombohedra isomorphous with crystallized alumina. Its density is then 5·21, but its density is lower when in the amorphous state. It melts in the fire of a furnace, forming a hard black crystalline mass.

The sesquioxide of chromium is green and is used for painting on porcelain. Charcoal and chlorine, separately, do not alter it at red heat, but a mixture of these two bodies destroys it at a high temperature, producing the perchloride of chromium and carbonic anhydride.

Acids act on it with difficulty. However, as a hydrate is known which corresponds to it and which possesses well-characterized basic properties, this oxide ought to be considered as a basic anhydride.

**Perhydrate of Chromium** $\left(\left.\begin{matrix}Cr^{2vi}\\H^6\end{matrix}\right\}O^6\right)$.—In order to prepare this body, chromate of potassium is dissolved in water strongly acidulated with hydrochloric acid, and a current of sulphurous anhydride is transmitted through the solution. This current must be continued during a sufficient time for the liquid, when placed in a stoppered bottle and well shaken, still to retain the sulphurous odour after twenty-four hours.

Under these conditions, and in consequence of the reducing action of the sulphurous anhydride, sulphate of potassium and sulphuric acid are produced along with hydrated perchloride of chromium, which colours the liquid green.



$$\underset{\text{Chromate of potassium.}}{2\left(\left.\begin{matrix}CrO^2\\K^2\end{matrix}\right\}O^2\right)} + \underset{\text{Hydrochloric acid.}}{6\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Sulphurous anhydride.}}{3\left(SO^2\right)} = \underset{\text{Sulphate of potassium.}}{2\left(\left.\begin{matrix}SO^{2\prime\prime}\\K^2\end{matrix}\right\}O^2\right)}$$

$$+ \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2\prime\prime}\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Perchloride of chromium.}}{\left(Cr^2Cl^6\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

When the transformation of the chromate of potassium is complete, ammonia is added to the liquid. Perhydrate of chromium is precipitated, which must be collected on a filter and carefully washed. It answers to the formula $\left(\left.\begin{matrix}Cr^{2vi}\\H^6\end{matrix}\right\}O^6 + 7\text{ aq.}\right)$.

This compound is soluble in cold alkaline solutions, but if these solutions be heated it is again precipitated in a different state of hydration from the first. Its formula is then $\left(\left.\begin{matrix}Cr^{2vi}\\H^6\end{matrix}\right\}O^6 + 6\text{ aq.}\right)$

Perhydrate of chromium readily dissolves in acids, giving salts of chromium. When strongly heated it is dehydrated, and becomes incandescent at red heat and transformed into anhydrous sesquioxide, which is insoluble in acids. In this property the hydrate of chromium resembles the hydrates of iron and aluminium.

The chromic hydrate and its corresponding salts present interesting allotropic modifications: this body takes different shades according to which modification of its sulphate it is extracted from; it is grey when precipitated from the violet sulphate, and bluish grey when from the green.

**Persulphate of Chromium** $\left(\left.\begin{matrix}(SO^{2\prime\prime})^3\\Cr^{2vi}\end{matrix}\right\}O^6\right)$.—When oxide of chromium arising from the desiccation of chromic hydrate at 100° is digested in 8 or 10 parts of sulphuric acid, at the end of some days a violet-coloured sulphate is obtained. This salt becomes green when its solution is boiled, and red when it is heated for some time to 200°.

Chloride of barium only partially precipitates the green sulphate, which always retains part of its sulphuryl.

**Chrome Alum** $\left(\left.\begin{matrix}(SO^{2\prime\prime})^3\\Cr^{2vi}\end{matrix}\right\}O^6 + \left.\begin{matrix}SO^{2\prime\prime}\\K^2\end{matrix}\right\}O^2 + 24\text{ aq.}\right)$.—Sulphate of chromium possesses the property of combining with alkaline sulphates; double salts are thus formed which crystallize with twenty-four molecules of water. These salts, which are isomorphous with alums, are therefore called chrome alums.

The double sulphate of potassium and chromium is obtained by making a mixture of chromate of potassium in aqueous solution, sulphuric acid, and alcohol. The mixture ought to be made slowly that it may not become too hot, otherwise the sulphate of chromium, instead of being produced in its violet modification, is produced in its green form and gives the green double sulphate which does not crystallize. If, however, the solution of this latter salt be left alone for a considerable time it undergoes a molecular transformation and changes to the state of violet crystallizable chrome alum.

The following equation shows the formation of chrome alum :

$$\underset{\text{Chromate of potassium.}}{4\left(\left.\begin{matrix}\mathrm{CrO^2}\\ \mathrm{K^2}\end{matrix}\right\}\mathrm{O^2}\right)} + \underset{\text{Sulphuric acid.}}{10\left(\left.\begin{matrix}\mathrm{SO^{2''}}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{O^2}\right)} + \underset{\text{Alcohol.}}{3\left(\left.\begin{matrix}\mathrm{C^2H^5}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Water.}}{23\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}$$

$$= \underset{\text{Acetic acid.}}{3\left(\left.\begin{matrix}\mathrm{C^2H^3O}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Sulphate of potassium.}}{2\left(\left.\begin{matrix}\mathrm{SO^{2''}}\\ \mathrm{K^2}\end{matrix}\right\}\mathrm{O^2}\right)} + 2\underbrace{\left[\left.\begin{matrix}\mathrm{(SO^{2''})^3}\\ \mathrm{Cr^{2vi}}\end{matrix}\right\}\mathrm{O^6},\ \left.\begin{matrix}\mathrm{SO^{2''}}\\ \mathrm{K^2}\end{matrix}\right\}\mathrm{O^2} + 24\,\mathrm{aq.}\right]}_{\text{Potassic chrome alum.}}$$

On replacing the chromate of potassium in this preparation by the chromate of sodium or of ammonium, sodic or ammoniacal chrome alum would be obtained.

Crystallized potassic chrome alum is violet; it crystallizes in octahedra and is isomorphous with the alums of aluminium and manganese. Water readily dissolves it, but it is insoluble in alcohol.

At 80° violet chrome alum is transformed into uncrystallizable green alum.

**Chromic Anhydride** ($CrO^3$).—An aqueous solution of bichromate of potassium saturated at boiling point is made. On cooling, 100 parts in volume of this liquid are added to from 120 to 150 volumes of sulphuric acid; the mixture at first becomes heated, and as it cools needles of chromic anhydride are deposited. The liquor is decanted; the needles are placed between two smooth porcelain plates and submitted to strong pressure for two or three days.

This body always contains a little sulphuric acid. To eliminate it, the crystals are dissolved in water and the solution shaken with a little chromate of barium, the sulphuric acid is precipitated as sulphate of barium, and an equivalent quantity of new chromic anhydride enters into the solution. When this has become clear by standing, it is decanted and crystallized in vacuo.

Chromic anhydride crystallizes in long needles of a beautiful red colour. Heat decomposes it into oxygen and sesquioxide of chromium; light acts in the same way, but slowly.

On account of the great instability of chromic anhydride it is a powerful oxidizer. Alcohol reduces it immediately, and can even take fire under its influence. Sulphurous anhydride and all reducing agents act in a similar manner.

Hydrochloric acid transforms this compound into water and perchloride of chromium, while chlorine is disengaged.

$$\underset{\text{Chromic anhydride.}}{2\left(\text{CrO}^3\right)} + \underset{\text{Hydrochloric acid.}}{12\left(\left.\begin{matrix}\text{H}\\ \text{Cl}\end{matrix}\right\}\right)} = \underset{\text{Perchloride of chromium.}}{\left(\text{Cr}^2\text{Cl}^6\right)} + \underset{\text{Chlorine.}}{3\left(\left.\begin{matrix}\text{Cl}\\ \text{Cl}\end{matrix}\right\}\right)} + \underset{\text{Water.}}{6\left(\left.\begin{matrix}\text{H}\\ \text{H}\end{matrix}\right\}\text{O}\right)}$$

In presence of bases that are readily oxidized, like ferrous hydrate, chromic acid is reduced and in consequence does not give salts.

Chromic acid $\left(\left.\begin{matrix}\text{CrO}^{2\prime\prime}\\ \text{H}^2\end{matrix}\right\}\text{O}^2\right)$ has not been obtained, but a whole class of salts representing this acid, in which the two atoms of hydrogen are replaced by metals, is known. The neutral salts answer to the formula $\left(\text{CrO}^{2\prime\prime}\left\{\begin{matrix}\text{OM}'\\ \text{OM}'\end{matrix}\right.\right)$,—(M′ being any monatomic metal). Acid salts may also be conceived which would answer to the formula $\left(\text{CrO}^{2\prime\prime}\left\{\begin{matrix}\text{OH}\\ \text{OM}'\end{matrix}\right.\right)$, but none of them have as yet been prepared.

The most important of the chromates is the chromate of potassium.

**Neutral Chromate of Potassium** $\left(\left.\begin{matrix}\text{CrO}^{2\prime\prime}\\ \text{K}^2\end{matrix}\right\}\text{O}^2\right)$.—The principal ore of chromium is a compound to which mineralogists have given the name of chrome iron-stone, and which answers to the formula $\left(\left.\begin{matrix}\text{Cr}^{2\text{vi}}\\ \text{Fe}''\end{matrix}\right\}\text{O}^4\right)$. When this ore is calcined with half its weight of nitrate of potassium, these two compounds react on each other, giving rise to chromate of potassium. The halogen residue of nitric acid contained in the nitrate of potassium here acts as a simple oxidizer.

The resulting mass is treated with water, and as this water, besides the chromate of potassium dissolves also silicate of the same metal arising from the quartz with which the ore was mixed, nitric acid must be added to precipitate the silica. Under the influence of this acid, the neutral chromate passes to the state of bichromate, which is separated by crystallization. The bichromate of potassium is then again dissolved in water, and for 297 parts of this salt 138 parts of carbonate of potassium are added; the liquid on evaporating leaves beautiful yellow crystals of neutral chromate of potassium.

$$\underset{\text{Bichromate of potassium.}}{\left(\begin{matrix}\text{CrO}^{2\prime\prime}\\ \\ \text{CrO}^{2\prime\prime}\end{matrix}\left\{\begin{matrix}\text{OK}\\ \text{O}\\ \text{OK}\end{matrix}\right\}\right)} + \underset{\text{Potassic carbonate.}}{\left(\text{CO}''\left\{\begin{matrix}\text{OK}\\ \text{OK}\end{matrix}\right.\right)} = \underset{\text{Carbonic anhydride.}}{\left(\text{CO}''.\text{O}\right)} + \underset{\text{Neutral chromate of potassium.}}{2\left(\text{CrO}^{2\prime\prime}\left\{\begin{matrix}\text{OK}\\ \text{OK}\end{matrix}\right.\right)}$$

The neutral chromate of potassium has strong colouring power, so that very small quantities of this salt are sufficient to colour large quantities of water yellow.

**Chlorinated Derivatives of Chromic Acid.** — A compound

$\left(CrO^{2''}\left\{\begin{matrix}OH\\Cl\end{matrix}\right.\right)$ is known which represents the normal chromic acid in which one hydroxyl is replaced by chlorine, the other remaining intact. This compound, which is called chromic chlorhydrin, only exists however when joined to two molecules of hydrochloric acid, as the formula $\left(CrO^{2''}\left\{\begin{matrix}OH\\Cl\end{matrix}\right., 2\left(\begin{matrix}H\\Cl\end{matrix}\right)\right)$ expresses. The hydrochloric acid appears to exist here in the same state as the water of crystallization in salts, and consequently we need not take it into account in explaining the atomic composition of the body.

Chromic chlorhydrin also containing an atom of typical hydrogen, may exchange it for a metal, and form salts. A body of this kind is known which contains potassium; its formula is $\left(CrO^{2''}\left\{\begin{matrix}OK\\Cl\end{matrix}\right.\right)$. It has been improperly called chromate of chloride of potassium. It is obtained by boiling chromate of potassium with hydrochloric acid, and on cooling the solution deposits beautiful red needles.

$$\underset{\text{Neutral chromate of potassium.}}{\left(CrO^{2''}\left\{\begin{matrix}OK\\OK\end{matrix}\right.\right)} + \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Chloride of potassium.}}{\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)} + \underset{\text{Chromate of chloride of potassium.}}{\left(CrO^{2''}\left\{\begin{matrix}OK\\Cl\end{matrix}\right.\right)}$$

A compound is also known which results from the substitution of two atoms of chlorine for the two halogen residues of the bases which act in neutral chromates. This body is improperly called chlorochromic acid; it ought to be named chloride of chromyl or chromic dichlorhydrin. Its formula is $\left(CrO^{2''}\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)$. It is decomposed on contact with water, producing hydrochloric acid and chromic anhydride.

$$\underset{\text{Chloride of chromyl.}}{\left(CrO^{2''}\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Chromic anhydride.}}{\left(CrO^{3}\right)} + \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)}$$

The chloride of chromyl is obtained by distilling a mixture of melted chloride of sodium, chromate of potassium, and sulphuric acid.

**Condensed Derivatives of Chromic Acid.**—Like polyatomic acids in general, and particularly like sulphuric acid, to which it corresponds in constitution, chromic acid possesses the property of being condensed. It is true that neither the dichromic acid $\left(\begin{matrix}CrO^{2''}\\CrO^{2''}\end{matrix}\left\{\begin{matrix}OH\\O\\OH\end{matrix}\right.\right)$ corresponding to the disulphuric acid is known, nor the trichromic acid $\left(\begin{matrix}CrO^{2''}\;\{OH\\CrO^{2''}\;\left\{\begin{matrix}O\\O\end{matrix}\right.\\CrO^{2''}\;\{OH\end{matrix}\right)$, but we know an acid which only differs from dichromic by the substitution of sulphuryl $(SO^{2''})$ for chromyl $(CrO^{2''})$.

This is the sulphochromic acid $\left(\begin{array}{ll} CrO^{2\prime\prime} & \Big\{ OH \\ & \quad O \\ SO^{2\prime\prime} & \Big\{ OH \end{array}\right)$. Salts also exist which are derived either from sulphochromic acid or from the unknown dichromic acid, or even from the trichromic acid. These are the potassic dichromate and the trichromate of the same metal.

**Potassic Dichromate** (*Bichromate of Potassium*) $\left(\begin{array}{ll} CrO^{2\prime\prime} & \Big\{ OK \\ & \quad O \\ CrO^{2\prime\prime} & \Big\{ OK \end{array}\right)$.—We have already seen how this salt is prepared when speaking of the neutral chromate of potassium. It is a body which crystallizes in beautiful orange-red crystals, which have as great a colouring property as the chromate of potassium.

**Potassic Trichromate** $\left(\begin{array}{ll} CrO^{2\prime\prime} & \Big\{ OK \\ & \quad O^{\prime\prime} \\ CrO^{2\prime\prime} & \Big\} \\ & \quad O^{\prime\prime} \\ CrO^{2\prime\prime} & \Big\{ OK \end{array}\right) = (Cr^3K^2O^{10})$.—This body is separated in beautiful pearly crystals of a reddish-black colour, when a solution of dichromate of potassium in ordinary nitric acid, saturated at 60°, is left to cool. This body becomes black in the air, boils between 145° and 150°, and has a density of 3·631.

**Perchromic Acid** ($CrH^2O^4$).—This acid is not certainly known. When oxygenated water is made to act on chromic acid, a substance is produced to which is attributed the composition of perchromic acid or anhydride; it is blue, soluble in ether, and very unstable.

**Sulphide of Chromium.**—Chromium combines with sulphur and forms a sesquisulphide of this metal ($Cr^2S^3$).

**Distinctive Characters of the Salts of Chromium.**—These salts are recognized by the following properties:

1st. With the soluble proto-salts, fixed alkalies give a deep-brown precipitate which becomes a clear brown. With per-salts they give a violet precipitate which is soluble in an excess of the reagent, but which is again deposited when the solution is boiled.

2nd. Hydrosulphuric acid does not precipitate either the per- or the proto-salts.

3rd. With proto-salts the alkaline sulphides give a black precipitate, and with per salts a greyish-green precipitate of per-hydrate.

4th. All the compounds of chromium, when calcined with a mixture of carbonate and nitrate of potassium, give a soluble chromate of potassium.

## COBALT Co.

Atomic weight = 59. Molecular weight unknown.

Cobalt may be obtained by reducing its oxide by charcoal at a high temperature; but it is obtained purer by calcining the oxalate of this metal:

$$\underset{\text{Oxalate of cobalt.}}{(C^2Co^{\prime\prime}O^4)} = \underset{\text{Carbonic anhydride.}}{2(CO^2)} + \underset{\text{Cobalt.}}{Co.}$$

Cobalt may also be prepared by the reduction of its oxide by means of hydrogen. When the reduction takes place at a relatively low temperature, the metal obtained is pyrophoric.

There is a third process by which cobalt may be obtained, consisting in the reduction of the chloride by hydrogen at an elevated temperature.

Cobalt is silver-white; it presents a fine grained fracture; its density is 8·50; it is very magnetic and only slightly malleable. Its fusing point is about equal to that of iron; it can be preserved for any length of time in the air and under water at the ordinary temperature; at an elevated temperature, on the contrary, it readily oxidizes.

This metal unites directly with chlorine, bromine, and iodine. It slowly dissolves in sulphuric and hydrochloric acids, disengaging hydrogen; nitric acid attacks it energetically.

Cobalt combines with two atoms of chlorine, bromine, iodine or fluorine, and forms the following compounds:

| | |
|---|---|
| Chloride of cobalt . . . . . . . | $CoCl^2$ |
| Bromide ,, . . . . . . . | $CoBr^2$ |
| Iodide ,, . . . . . . . | $CoI^2$ |
| Fluoride ,, . . . . . . . | $CoFl^2$ |

Besides these, when sesquioxide of cobalt is dissolved in hydrochloric acid, a red liquid is formed which disengages chlorine on the slightest elevation of temperature. It is generally admitted that this liquid contains a chloride of cobalt ($Co^2Cl^6$).

With oxygen cobalt forms:

| | |
|---|---|
| A protoxide. . . . . . . . . . | $CoO$ |
| A sesquioxide . . . . . . . . . | $Co^2O^3$ |
| A saline oxide. . . . . . . . . | $Co^3O^4$ |

The hydrate $\left(\left.\begin{matrix}Co''\\H^2\end{matrix}\right\}O^2\right)$ corresponds to the protoxide. This hydrate may exchange its two atoms of typical hydrogen for acid radicles and form proto-salts of cobalt.

A hydrate $\left(\left.\begin{matrix}Co^{2vi}\\H^6\end{matrix}\right\}O^6\right)$ ought to correspond to the sesquioxide, but it is unknown; the second anhydride $\left(\left.\begin{matrix}Co^{2vi}\\H^2\end{matrix}\right\}O^4\right)$ alone exists. The sesquioxide of cobalt dissolves in acids, especially in acetic acid, forming per-salts which are very unstable; by the action of heat they lose oxygen, and are transformed into proto-salts. There are three sulphides of cobalt known, corresponding to three of the sulphides of iron. They are:

| | |
|---|---|
| The protosulphide of cobalt . . . | $CoS$ |
| The sesquisulphide . . . . . . . | $Co^2S^3$ |
| The bisulphide . . . . . . . . | $CoS^2$ |

Cobalt can also combine with phosphorus and arsenic.

From the preceding remarks, it may be concluded that the tetratomicity of the salts of cobalt is somewhat doubtful, this metal always acting as bivalent, and those of its compounds in which it acts with a greater atomicity being so unstable that their formula cannot be fixed with certainty, with the exception of the sesquioxide, which proves nothing on account of the biatomicity of oxygen.

Nevertheless, as the per-compounds of metals of this series diminish in stability the further these metals remove from aluminium to approach cobalt and nickel; as, after all, though their composition cannot be established with certainty, the analogies of cobalt with iron and manganese leave no doubt as to the formula of its per-salts, cobalt can scarcely be separated from the other metals of this group, and its atomicity ought to be considered as equal to four.

The resemblance between cobalt and iron, and the tetratomicity of the first of these metals, become evident when their cyanogen compounds, of which we shall speak in organic chemistry, are considered.

**Reactions of the Salts of Cobalt.**—The salts of cobalt are recognized by the following properties:

1st. They are all of a reddish colour: one, the chloride, becomes blue when heated, and regains its original colour on cooling. From this property this salt is used as a sympathetic ink, its blue colour prevailing in sufficient intensity over the red to enable its diluted solution to give invisible characters, which appear blue when heated.

2nd. In the solution of these salts fixed alkalies give a lavender-blue precipitate of proto-hydrate of cobalt.

3rd. Ammonia produces an analogous reaction, but the precipitation is incomplete, and would not take place at all in presence of an excess of acid or of an ammoniacal salt. The ammoniacal solution thus obtained is not precipitated by potash; but if it be exposed to the air after being treated by this alkali it soon deposits hydrated sesquioxide of cobalt. Cobalt may also be precipitated by the sulphide of ammonium.

4th. Hydrosulphuric acid does not precipitate the salts of cobalt.

5th. Alkaline sulphides give a black precipitate of sulphide of cobalt which is insoluble in acetic acid and in dilute hydrochloric acid.

6th. Alkaline carbonates produce a rose-coloured precipitate of carbonate of cobalt in the aqueous solution of its salts.

7th. The compounds of cobalt give a blue bead when heated before the blowpipe with borax.

## NICKEL Ni.

Atomic weight = 59. Molecular weight unknown.

Nickel is obtained in a metallic state by processes that are absolutely identical with those used for cobalt.

This metal is silver-white; it is malleable and ductile, very magnetic at the ordinary temperature, but loses this property at 350°; its density is 8·666. It is about as fusible as manganese. Charcoal forms with nickel a compound more fusible than the pure metal, analogous to cast iron. Nickel is not affected by the air; at a high temperature it burns in oxygen. Dilute hydrochloric and sulphuric acids dissolve it, disengaging hydrogen. Nitric acid also dissolves it.

Nickel has been used in the arts for the last few years. It enters into the composition of Belgian and Swiss copper money, and also of packfong (German silver), which alloy contains 50 parts of copper, 25 of nickel, and 25 of zinc; it is used in clockwork, etc.

A single combination of nickel with each of the halogen metalloids is known. This combination corresponds to the formula ($NiR'^2$). Oxygen unites with nickel in two proportions, and forms the protoxide ($NiO$) and the sequioxide ($Ni^2O^3$). A hydrate $\left(\left.\begin{matrix}Ni''\\H^2\end{matrix}\right\} O^2\right)$ correponds to the protoxide. The hydrogen of this hydrate can be replaced by acid radicles, and salts of nickel formed, which might be called proto-salts. The sesquioxide loses oxygen in presence of acids, being ransformed into proto-salts, and chlorine is disengaged on its contact with hydrochloric acid, giving protochloride. No salt of nickel corresponding to the sesquioxide is known.

The simple sulphate and the double sulphates which nickel forms re isomorphous, not only with the sulphates of cobalt, but also with the protosulphates of iron and manganese, and with those of the metals of the magnesian series.

The tetratomicity of nickel is still more difficult to establish than hat of cobalt. Here we have only a single compound on which his tetratomicity can be based, the sesquioxide, an unstable body, ncapable of forming salts, capable of being considered as resulting om the aggregation of several molecules of oxygen, and consequently roving nothing. On the other hand, nickel greatly resembles zinc, agnesium, etc. It would therefore appear more rational, at first ght, to class it among biatomic instead of tetratomic metals. Neverheless, as the reasons we gave when treating of cobalt caused us to ass this latter body with iron, the great analogy between nickel and obalt compels us also to place nickel among the tetratomic metals, bserving that if its absolute or true atomicity be equal to 4, its appant or manifest atomicity is never equal to more than 2.

**Distinctive Characters of Salts of Nickel.**—The distinctive characrs of salts of nickel are the following:

1st. These salts are of an emerald-green colour.

2nd. Fixed alkalies produce in their solutions an apple-green precipitate of hydrate of nickel.

3rd. Ammonia partially precipitates perfectly neutral salts of ckel. If these salts are acid, or contain an ammoniacal salt, amonia does not precipitate them. When precipitation takes place, e precipitate dissolves in an excess of the reagent, and the liquid comes blue.

4th. Hydrosulphuric acid does not precipitate them; the alkaline sulphides produce a black precipitate, which is insoluble in acetic acid and in dilute hydrochloric acid.

5th. The cyanide of potassium produces a precipitate soluble in an excess of the reagent. The precipitate will be reproduced if the liquid be saturated by sulphuric acid. This property distinguishes nickel from cobalt. With salts of the latter metal the cyanide of potassium forms a precipitate soluble in an excess of the reagent; but when the precipitate is once dissolved, sulphuric acid does not cause it to reappear.

## LEAD Pb.

Atomic weight = 207. Molecular weight unknown.

Lead is generally extracted from its sulphide, known under the name of galena. There are different methods of extracting it:

1st, the ore is imperfectly roasted; a part of the sulphide is transformed into sulphate of lead:

$$\underset{\text{Sulphide of lead.}}{(PbS)} + \underset{\text{Oxygen.}}{2\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\right)} = \underset{\text{Sulphate of lead.}}{(SPbO^4)}$$

A second part forms oxide of lead and sulphurous anhydride:

$$\underset{\text{Sulphide of lead.}}{2(PbS)} + \underset{\text{Oxygen.}}{3\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\right)} = \underset{\text{Sulphurous anhydride.}}{2(SO^2)} + \underset{\text{Oxide of lead.}}{2(PbO)}$$

A third portion remains in the state of unattacked sulphide of lead.

When the oxidation is considered to be sufficiently advanced for the mass to contain the required proportions of oxide, sulphate, and sulphide, the access of air is arrested, and the mass is strongly heated. The sulphate and oxide of lead react on the sulphide; sulphurous anhydride is disengaged, and metallic lead remains.

$$\underset{\text{Sulphide of lead.}}{(PbS)} + \underset{\text{Sulphate of lead.}}{(SPbO^4)} = \underset{\text{Sulphurous anhydride.}}{2(SO^2)} + \underset{\text{Lead.}}{2Pb}$$

$$\underset{\text{Sulphide of lead.}}{(PbS)} + \underset{\text{Oxide of lead.}}{2(PbO)} = \underset{\text{Sulphurous anhydride.}}{(SO^2)} + \underset{\text{Lead.}}{3Pb}$$

The lead may also be extracted by entirely transforming the sulphide into oxide by roasting, and then reducing the oxide by charcoal, or by directly heating galena with iron, which combines with the sulphur and liberates lead.

Lead is of a bluish-grey colour; it presents a metallic aspect when newly-cut, but readily tarnishes in air. It is soft, and leaves traces on paper when drawn along it.

The density of pure lead is 11·445, which, instead of increasing by hammering, as is the case with other metals, diminishes. Lead crystallizes in regular octahedra or in pyramids with four faces. These crystals may be artificially obtained.

Lead melts at 334°, and may be volatilized by the blowpipe. This metal is the sixth in rank for malleability, and the eighth for ductility. Its tenacity is very slight.

Melted lead can dissolve a small quantity of oxide, which renders it brittle, but it loses this property by being stirred with charcoal while melted. It may be kept for any length of time in air; a slight layer of oxide appears to be formed on its surface, but this preserves the remaining metal against any further oxidation: when heated, lead readily oxidizes.

When lead is left in pure water exposed to the air, the metal absorbs oxygen and carbonic anhydride, and gives an hydrated carbonate of lead. Soluble salts, especially the sulphate of calcium, prevent this reaction taking place, and thereby preserve ordinary water-pipes from oxidation.

Hydrochloric acid and dilute sulphuric acid do not perceptibly affect lead, but concentrated sulphuric acid attacks it, disengaging sulphurous anhydride and forming sulphate of lead. The best solvent for lead is nitric acid.

Lead easily combines with mercury and forms an amalgam, which is either liquid or solid, according as the mercury or lead predominates.

Lead is tetratomic. It can combine with four molecules of two organic monatomic radicles, methyl and ethyl; we know:

| | |
|---|---|
| Lead-ethyl . . . . . . . . . . . | $(Pb(C^2H^5)'^4)$. |
| Lead-methyl . . . . . . . . . | $(Pb(CH^3)'^4)$. |

The formula of these compounds is not doubtful; the fourth part of ethyl or methyl therein may be replaced by chlorine or by iodine, which would be impossible if they contained less than four molecules of these radicles.

With simple monatomic bodies, lead always acts as bivalent, which means that it is never saturated. There exist:

| | |
|---|---|
| A chloride of lead . . . . . . . . . | $PbCl^2$. |
| A bromide . . . . . . . . . . . . . | $PbBr^2$. |
| An iodide . . . . . . . . . . . . . . | $PbI^2$. |
| A fluoride . . . . . . . . . . . . . . | $PbFl^2$. |

Lead also combines with biatomic metalloids: it forms a single compound with sulphur, the sulphide of lead $Pb''S$.

It combines in different proportions with oxygen. We find four distinct oxides:

| | |
|---|---|
| The suboxide . . . . . . . . . . . . . | $\mathrm{Pb^2O}$. |
| The protoxide . . . . . . . . . . . . | $\mathrm{Pb''O}$. |
| Minium or red lead . . . . . . . . . | $\mathrm{Pb^3O^4}$. |
| And the binoxide (plumbic anhydride) . . . | $\mathrm{Pb^{IV}O^2}$. |

In the two last of these oxides lead acts with its maximum atomicity.

A condensed hydrate $\left(\begin{array}{ll} \mathrm{Pb}'' & \left\{\begin{array}{l}\mathrm{OH}\\ \mathrm{O}\end{array}\right. \\ \mathrm{Pb}'' & \left\{\mathrm{OH}\right. \end{array}\right)$ to which salts correspond, is classed with the protoxide. The simple hydrate $\left(\mathrm{Pb}''\left\{\begin{array}{l}\mathrm{OH}\\ \mathrm{OH}\end{array}\right.\right)$ has not yet been obtained, but a great number of salts are known which result from the substitution of acid radicles for the typical hydrogen of this base.

## Haloid Compounds of Lead.

**Chloride of Lead** $\left(\mathrm{Pb}''\left\{\begin{array}{l}\mathrm{Cl}\\ \mathrm{Cl}\end{array}\right.\right)$.—The chloride of lead may be prepared by heating the oxide of lead with hydrochloric acid. A white powder is thus obtained, which when dissolved in boiling water crystallizes on cooling in beautiful acicular crystals having a silvery lustre. This salt may also be prepared by adding hydrochloric acid or a soluble chloride to the cold solution of a salt of lead.

$$\text{1st.}\ \underset{\text{Oxide of lead.}}{(\mathrm{PbO})} + 2\underset{\text{Hydrochloric acid.}}{\left(\begin{array}{l}\mathrm{H}\\ \mathrm{Cl}\end{array}\right\}\Big)} = \underset{\text{Chloride of lead.}}{(\mathrm{Pb''Cl^2})} + \underset{\text{Water.}}{\left(\left.\begin{array}{l}\mathrm{H}\\ \mathrm{H}\end{array}\right\}\mathrm{O}\right)}$$

$$\text{2nd.}\ \underset{\text{Neutral nitrate of lead.}}{\left(\mathrm{Pb}''\left\{\begin{array}{l}\mathrm{ONO^2}\\ \mathrm{ONO^2}\end{array}\right.\right)} + 2\underset{\text{Chloride of sodium.}}{\left(\left.\begin{array}{l}\mathrm{Na}\\ \mathrm{Cl}\end{array}\right\}\right)} = 2\underset{\text{Sodic nitrate.}}{\left(\left.\begin{array}{l}\mathrm{NO^2}\\ \mathrm{Na}\end{array}\right\}\mathrm{O}\right)} + \underset{\text{Chloride of lead.}}{\left(\mathrm{Pb}''\left\{\begin{array}{l}\mathrm{Cl}\\ \mathrm{Cl}\end{array}\right.\right)}$$

Chloride of lead is very sparingly soluble in cold water, but more so in boiling water; alcohol does not dissolve it at all.

Chloride of lead melts at red heat, and if heated still higher emits abundant fumes. When melted and cooled, it forms a translucent mass which may be cut by a knife.

In the arts, compounds of chloride and oxide of lead, oxychlorides, the exact atomic composition of which is unknown, are used for paints. These products all have a yellow colour.

**Bromide of Lead** ($\mathrm{PbBr^2}$).—This is obtained by double decomposition by means of a soluble salt of lead and a soluble bromide; it is insoluble in alcohol, very slightly soluble in cold, but more soluble in boiling water. Like the chloride, it crystallizes in beautiful scales from a saturated solution in boiling water.

**Iodide of Lead** ($\mathrm{PbI^2}$).—This is prepared like the bromide and the chloride, with the exception that in the reaction a soluble iodide is substituted for the chloride or bromide.

Iodide of lead is yellow, insoluble in alcohol, very slightly soluble in cold but more readily in boiling water. When this solution is cooled, the salt crystallizes in beautiful golden-yellow scales. Melted in the air, it is transformed into an oxyiodide, losing iodine. When heated with exclusion of the air, it becomes reddish yellow, then brick red, then brownish red, and it finally melts into a liquid of the same colour, which on cooling becomes a yellow solid. Iodide of lead combines with hydrochloric acid, with the iodides of potassium and ammonium, etc., forming double salts; with ammonia it forms the iodide of plombo-diammonium ($[Pb''H^6N^2]I^2$).

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### Combinations of Lead with Biatomic Metalloids.

**Sulphide of Lead** (PbS) (*Galena*).—This is the most abundant ore of lead. Sulphide of lead can also be obtained artificially by causing hydrosulphuric acid to act on the solution of a soluble salt of lead.

$$\underset{\text{Neutral sulphate of lead.}}{\left(Pb''\left\{\begin{matrix}ONO^2\\ONO^2\end{matrix}\right.\right)} + \underset{\text{Hydrosulphuric acid.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}S\right)} = \underset{\text{Nitric acid.}}{2\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)} + \underset{\text{Sulphide of lead.}}{\left(Pb''S\right)}$$

The sulphide of lead prepared by double decomposition, constitutes a black amorphous powder. Galena, on the contrary, crystallizes in the cubic system. Its crystals are of a bluish-grey colour and possess a metallic lustre. Its density is from 7·25 to 7·7; it melts at red heat and can even be slightly volatilized.

We have already seen that when galena is roasted, sulphurous anhydride is formed and oxide and sulphate of lead; we have also seen that galena when heated with either oxide or sulphate of lead, and protected from the air, gives sulphurous anhydride and metallic lead.

Neither hydrochloric acid nor dilute sulphuric acid attack galena; but the latter acid when concentrated yields oxygen to the galena, which passes to the state of sulphate, and the acid is decomposed into water and sulphurous anhydride.

Dilute nitric acid transforms galena into nitrate of lead, with deposition of sulphur arising from the hydrosulphuric acid which is first ormed, and which the nitric acid afterwards decomposes.

$$\underset{\text{Sulphide of lead.}}{\left(PbS\right)} + \underset{\text{Nitric acid.}}{2\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)} = \underset{\text{Nitrate of lead.}}{\left(Pb''\left\{\begin{matrix}ONO^2\\ONO^2\end{matrix}\right.\right)} + \underset{\text{Hydrosulphuric acid.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}S\right)}$$

If the nitric acid be concentrated, a part of the deposited sulphur ecomes oxidized, sulphuric acid is formed, and this acid precipitates an equivalent quantity of lead in the state of insoluble sulphate. The same products are therefore obtained as with the dilute acid, with the addition of the sulphate of lead. If the acid is at the maximum of concentration, all the sulphur passes to the state of sulphuric acid, and in consequence only the sulphate of lead is obtained.

Galena is often argentiferous; the ores richest in silver are those crystallized in small crystals.

Besides the sulphide of lead ($PbS$), there appears to exist a sulphide ($Pb^2S$) and another sulphide ($Pb^4S$). The former sulphide is formed during the metallurgic treatment of galena. It may also be prepared by melting two atoms of lead with one atom of sulphur. The latter sulphide is obtained by calcining 100 parts of galena with 84 parts of lead.

**Protoxide of Lead** ($PbO$).—When lead is heated in air, a yellow powder is formed, which is called massicot, and which is protoxide of lead. Massicot is also formed when carbonate or nitrate of lead is submitted to careful calcination. If massicot be melted, it crystallizes on cooling, and is then called *litharge*.

Oxide of lead assumes various shades; for instance, if litharge be heated, instead of remaining reddish yellow, it becomes bright yellow, regaining its original colour on cooling. Litharge decomposes alkaline salts, liberating caustic alkali; for this effect it is necessary that the oxide of lead be in excess. When litharge is boiled with a highly-concentrated solution of potash, it is dissolved. When the liquid cools, the oxide is again deposited in very heavy small crystals.

The protoxide of lead melted and submitted to a red heat absorbs oxygen, which, like metallic silver, it gives off on cooling. If heated in an earthen crucible, it combines with the silica contained in this crucible, forming a fusible silicate, and speedily penetrates and destroys the crucible.

Protoxide of lead enters into double decomposition with acids, and gives very stable salts of lead, it is therefore a basic anhydride. We have just seen that it can also dissolve in alkaline liquids and sometimes act as acid anhydride. Nevertheless, its basic are very much stronger than its acid properties.

When protoxide of lead is heated for a long time in air without being melted, minium is formed.

**Hydrate of Lead** $\left(Pb\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)$.—This hydrate is not known, but there is a large number of salts corresponding to it, the most important of which are the sulphate, nitrate, chromate, acetate, and carbonate.

**Sulphate of Lead** $\left(\begin{matrix}SO^{2''}\\Pb''\end{matrix}\right\}O^2\Big)$.—In manufactories where woven goods are printed, acetate of aluminium is prepared by precipitating the sulphate of aluminium by acetate of lead; sulphate of lead is formed in this reaction as an accessory product.

$$\underset{\text{Aluminic sulphate.}}{\left(\left.\begin{matrix}(SO^{2''})^3\\ Al^{2vi}\end{matrix}\right\} O^6\right)} + \underset{\text{Acetate of lead.}}{3\left(Pb''\left\{\begin{matrix}OC^2H^3O\\ OC^2H^3O\end{matrix}\right.\right)} = \underset{\text{Acetate of aluminium.}}{\left(\left.\begin{matrix}Al^{2vi}\\ (C^2H^3O)^6\end{matrix}\right\} O^6\right)}$$

$$+ \underset{\text{Sulphate of lead.}}{3\left(\left.\begin{matrix}SO^{2''}\\ Pb''\end{matrix}\right\} O^2\right)}$$

Sulphate of lead forms a white powder, which is insoluble in water, and slightly soluble in acid liquids. Ammoniacal salts dissolve it, entering into double decomposition with it. Of all the salts of ammonium, the tartrate is the best solvent of the sulphate of lead.

Sulphate of lead cannot be decomposed by heat alone, a property which clearly distinguishes it from the sulphates of all the ordinary metals. Iron, zinc, and charcoal reduce it. With charcoal, the sulphate of lead is converted—according to the proportions in which these two bodies are mixed, and the greater or less rapidity with which they are heated, —into sulphide or sub-sulphide of lead, or even into metallic lead; in the two latter cases sulphurous anhydride is disengaged.

Boiled with a solution of carbonate of sodium, sulphate of lead is converted into carbonate, while the sodium passes to the state of sulphate.

If a mixture of one molecule of sulphate of lead and half a molecule of lime be moistened and left alone, hydrate of lead is formed which can be dissolved in acetic acid and transformed into acetate.

**Nitrate of Lead** $\left(Pb''\left\{\begin{matrix}ONO^2\\ ONO^2\end{matrix}\right.\right)$.—This nitrate is prepared by dissolving metallic lead or its oxide, in boiling nitric acid. The salt, being very slightly soluble in acid, is precipitated as it is formed. It is dissolved in water and crystallized.

Nitrate of lead dissolves more readily in hot water than in cold. Alcohol does not dissolve it. Heat decomposes it into oxygen, hyponitride and oxide of lead. When boiled with oxide of lead, it is transformed into a basic salt, answering to the formula $\left(Pb''\left\{\begin{matrix}ONO^2\\ OH\end{matrix}\right.\right)$.

$$\underset{\text{Neutral nitrate of lead.}}{\left(Pb''\left\{\begin{matrix}ONO^2\\ ONO^2\end{matrix}\right.\right)} + \underset{\text{Oxide of lead.}}{(PbO)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\} O\right)} = \underset{\text{Basic nitrate of lead.}}{2\left(Pb''\left\{\begin{matrix}ONO^2\\ OH\end{matrix}\right.\right)}$$

Heated with metallic lead and water, it is transformed into a nitrite with a great excess of metal. This nitrite, submitted to the action of a current of carbonic anhydride, gives carbonate and neutral nitrite of lead.

$$\text{1st.}\quad \underset{\text{Neutral nitrate of lead.}}{\left(Pb''\left\{\begin{matrix}ONO^2\\ ONO^2\end{matrix}\right.\right)} + \underset{\text{Lead.}}{2\,Pb} = \underset{\text{Triplumbic nitrite.}}{\left(\left.\begin{matrix}Pb'' & \{ONO\\ Pb'' & \{O\\ & \{O\\ Pb'' & \{ONO\end{matrix}\right\}\right)}$$

2nd. $$\underset{\text{Triplumbic nitrite.}}{\left(\left.\begin{matrix}\text{Pb}''\left\{\text{ONO}\right.\\ \text{Pb}''\left\{\begin{matrix}\text{O}\\ \text{O}\end{matrix}\right.\\ \text{Pb}''\left\{\text{ONO}\right.\end{matrix}\right\}\right)} + 2\underset{\text{Carbonic anhydride.}}{\left(\text{CO}^2\right)} = 2\underset{\text{Carbonate of lead.}}{\left(\left.\begin{matrix}\text{CO}''\\ \text{Pb}''\end{matrix}\right\}\text{O}^2\right)} + \underset{\text{Neutral nitrite of lead.}}{\left(\text{Pb}''\left\{\begin{matrix}\text{ONO}\\ \text{ONO}\end{matrix}\right.\right)}$$

**Chromate of Lead** $\left(\left.\begin{matrix}\text{CrO}^{2''}\\ \text{Pb}''\end{matrix}\right\}\text{O}^2\right)$.—Chromate of lead is prepared from the acetate of lead and potassic chromate or bichromate by double decomposition.

$$\underset{\text{Chromate of potassium.}}{\left(\left.\begin{matrix}\text{CrO}^{2''}\\ \text{K}^2\end{matrix}\right\}\text{O}^2\right)} + \underset{\text{Acetate of lead.}}{\left(\text{Pb}''\left\{\begin{matrix}\text{OC}^2\text{H}^3\text{O}\\ \text{OC}^2\text{H}^3\text{O}\end{matrix}\right.\right)} = \underset{\text{Chromate of lead.}}{\left(\left.\begin{matrix}\text{CrO}^{2''}\\ \text{Pb}''\end{matrix}\right\}\text{O}^2\right)} + 2\underset{\text{Acetate of potassium.}}{\left(\left.\begin{matrix}\text{C}^2\text{H}^3\text{O}\\ \text{K}\end{matrix}\right\}\text{O}\right)}$$

Chromate of lead is found native as a red substance crystallized in oblique rhomboid prisms (the red lead of mineralogists).

Artificial chromate is of a beautiful yellow colour, used by painters under the name of chrome yellow: if heated to redness it melts, and on cooling becomes a reddish mass.

When instead of precipitating the neutral chromate of potassium by the neutral acetate of lead, liquids which are not neutral are precipitated, the precipitate has a variable colour. The colour may also be varied according to the temperature at which the precipitation takes place. Generally the redder the chromates of lead the more are they charged with metal.

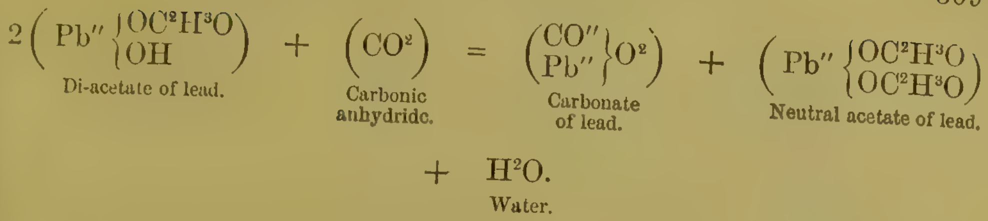
**Neutral Acetate of Lead** $\left(\text{Pb}''\left\{\begin{matrix}\text{OC}^2\text{H}^3\text{O}\\ \text{OC}^2\text{H}^3\text{O}\end{matrix}\right. + 3\ \text{aq.}\right)$.—When lead is left to the simultaneous action of air and the vapour of acetic acid, a basic acetate of lead is formed, which when dissolved in acetic acid in excess, gives a liquid which on evaporating deposits beautiful crystals, whose formula is $\left(\text{Pb}''\left\{\begin{matrix}\text{OC}^2\text{H}^3\text{O}\\ \text{OC}^2\text{H}^3\text{O}\end{matrix}\right. + 3\ \text{aq.}\right)$

The same salt may be obtained by dissolving litharge in acetic acid.

The neutral acetate of lead is extremely soluble in water. Ammonia does not precipitate it, because with the salts of lead this alkali gives not the hydrate, but sub-salts of lead, and the sub-acetates of lead are soluble.

The aqueous solution of neutral acetate of lead readily dissolves litharge when hot, and in this case either a simple bibasic salt or polyplumbic salts form. All these salts, when submitted to the action of a current of carbonic anhydride, give a precipitate of carbonate of lead, while the neutral acetate of the same metal is reformed.

$$\underset{\text{Neutral acetate of lead.}}{\left(\text{Pb}''\left\{\begin{matrix}\text{OC}^2\text{H}^3\text{O}\\ \text{OC}^2\text{H}^3\text{O}\end{matrix}\right.\right)} + \underset{\text{Oxide of lead.}}{\left(\text{PbO}\right)} + \underset{\text{Water.}}{\left(\text{H}^2\text{O}\right)} = 2\underset{\text{Bibasic acetate (di-acetate) of lead.}}{\left(\text{Pb}\left\{\begin{matrix}\text{OC}^2\text{H}^3\text{O}\\ \text{OH}\end{matrix}\right.\right)}$$

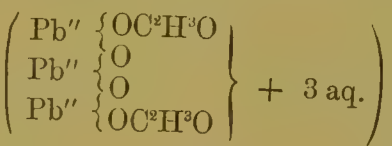


$$\underset{\text{Di-acetate of lead.}}{2\left(\mathrm{Pb''}\begin{cases}\mathrm{OC^2H^3O}\\ \mathrm{OH}\end{cases}\right)} + \underset{\text{Carbonic anhydride.}}{\left(\mathrm{CO^2}\right)} = \underset{\text{Carbonate of lead.}}{\left(\left.\begin{matrix}\mathrm{CO''}\\ \mathrm{Pb''}\end{matrix}\right\}\mathrm{O^2}\right)} + \underset{\text{Neutral acetate of lead.}}{\left(\mathrm{Pb''}\begin{cases}\mathrm{OC^2H^3O}\\ \mathrm{OC^2H^3O}\end{cases}\right)} + \underset{\text{Water.}}{\mathrm{H^2O}}.$$

**Neutral Carbonate of Lead** $\left(\left.\begin{matrix}\mathrm{CO''}\\ \mathrm{Pb''}\end{matrix}\right\}\mathrm{O^2}\right)$.—Native carbonate of lead is found in crystals of the fourth system. In the laboratory this body is obtained in the form of a fine white powder, by precipitating a solution of carbonate of sodium by a solution of acetate of lead. Carbonate of lead (white lead), being much used by painters, is manufactured upon a large scale. It is obtained by two processes: one, the Dutch method, is old; the modern method was discovered by Thénard, and is the Clichy process. In the Dutch method a jar containing a sheet of lead coiled in a spiral form is filled with vinegar, lightly covered with a plate of lead, and imbedded in decomposing dung, at a temperature of 35° or 40°. The coil of lead is thus submitted to the simultaneous action of air, vapours of acetic acid and of carbonic anhydride, which latter is produced from the decomposing hot-bed.

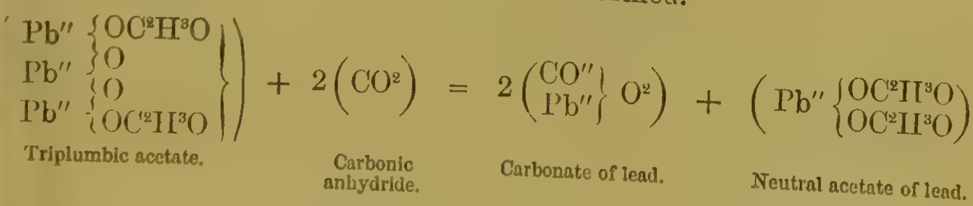
Under the influence of the air and vinegar, the lead first becomes covered with basic acetate, which on contact with carbonic anhydride forms neutral acetate and gives carbonate of lead; from time to time the layers of carbonate adhering to the coil of metal are detached, and washed to free it from the acetate it contains. It is then dried and powdered.

In the Clichy process, litharge is dissolved in acetic acid so as to obtain the triplumbic acetate.



$$\left(\left.\begin{matrix}\mathrm{Pb''}\left\{\mathrm{OC^2H^3O}\right.\\ \mathrm{Pb''}\begin{cases}\mathrm{O}\\ \mathrm{O}\end{cases}\\ \mathrm{Pb''}\left\{\mathrm{OC^2H^3O}\right.\end{matrix}\right\} + 3\text{ aq.}\right)$$

The solution of this salt is submitted to the action of a current of carbonic anhydride, two molecules of oxide of lead are separated in the state of carbonate, and neutral acetate is reformed.



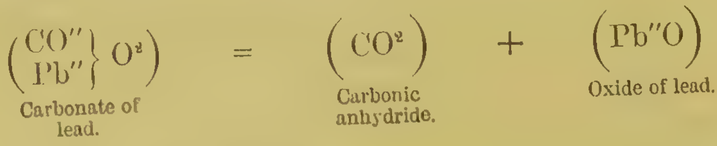
$$\underset{\text{Triplumbic acetate.}}{\left(\left.\begin{matrix}\mathrm{Pb''}\left\{\mathrm{OC^2H^3O}\right.\\ \mathrm{Pb''}\begin{cases}\mathrm{O}\\ \mathrm{O}\end{cases}\\ \mathrm{Pb''}\left\{\mathrm{OC^2H^3O}\right.\end{matrix}\right\}\right)} + \underset{\text{Carbonic anhydride.}}{2\left(\mathrm{CO^2}\right)} = \underset{\text{Carbonate of lead.}}{2\left(\left.\begin{matrix}\mathrm{CO''}\\ \mathrm{Pb''}\end{matrix}\right\}\mathrm{O^2}\right)} + \underset{\text{Neutral acetate of lead.}}{\left(\mathrm{Pb''}\begin{cases}\mathrm{OC^2H^3O}\\ \mathrm{OC^2H^3O}\end{cases}\right)}$$

This neutral acetate when boiled with litharge furnishes a fresh uantity of triplumbic acetate, which is again brought to the state of eutral carbonate, so that with the exception of inevitable loss by aste the same quantity of acetic acid serves for any length of time.

The Clichy white lead is inferior as a pigment to that prepared by the Dutch method, because it is composed of transparent crystalline particles, but if it be boiled with a little carbonate of potassium it will be found equal to the Dutch pigment.

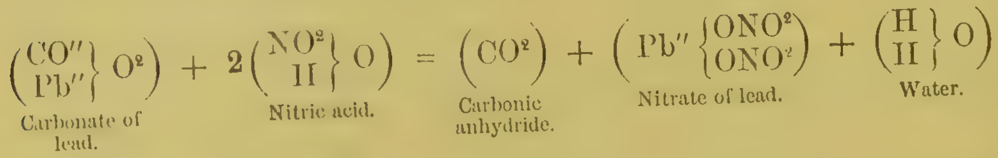
The workmen who manufacture white lead are exposed to the dangers of lead-poisoning (*see* Characters of Salts of Lead). Messrs. Pallu and Delaunay have introduced such improvements in their manufactory at Portillon, near Tours, that in this establishment these accidents no longer occur.

Under the influence of heat, carbonate of lead is decomposed into oxide of lead and carbonic anhydride.



$$\underset{\text{Carbonate of lead.}}{\left(\left.\begin{matrix}CO''\\Pb''\end{matrix}\right\}O^2\right)} = \underset{\text{Carbonic anhydride.}}{\left(CO^2\right)} + \underset{\text{Oxide of lead.}}{\left(Pb''O\right)}$$

It dissolves in acids, disengaging carbonic anhydride, water and a salt of lead being formed.



$$\underset{\text{Carbonate of lead.}}{\left(\left.\begin{matrix}CO''\\Pb''\end{matrix}\right\}O^2\right)} + 2\underset{\text{Nitric acid.}}{\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)} = \underset{\text{Carbonic anhydride.}}{\left(CO^2\right)} + \underset{\text{Nitrate of lead.}}{\left(Pb''\left\{\begin{matrix}ONO^2\\ONO^2\end{matrix}\right.\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

Sulphuretted hydrogen blackens it like all the other salts of lead, forming sulphide of lead, which causes painting by white lead to be readily affected. To restore its original colour it has been recommended to submit the painting blackened by sulphuretted hydrogen to the action of oxygenated water. The sulphide of lead is thus changed into sulphate, which is white like the carbonate.

**Diplumbic Hydrate** $\left(\begin{matrix}Pb'' & \left\{OH\right. \\ & O \\ Pb'' & \left\{OH\right.\end{matrix}\right)$.—This body is obtained by precipitating a soluble salt of lead by potash. The hydrate of lead is soluble in seven thousand times its weight of water; alkalies in excess readily dissolve it. It is white, but when heated it loses water and is transformed into an anhydrous protoxide of a red colour.

**Binoxide of Lead (Plumbic Anhydride)** ($PbO^2$).—Minium, as we shall see, may be considered as a plumbate of lead. When treated by acids it yields the elements of protoxide of lead, and a puce-coloured powder remains, which, when washed and dried, constitutes plumbic anhydride ($PbO^2$).

The same body is prepared by causing hypochlorous acid to act on the protoxide of lead suspended in water.

Binoxide of lead is an acid anhydride; it combines with bases and gives crystallized salts. M. Fremy, by heating this body with potassic hydrate, has obtained a crystallized plumbate of potassium, to which he attributes the formula ($PbO^2,K^2O + 3$ aq.), but it would be better to write it $\left(\left.\begin{matrix}Pb^{iv}\\ K^2\\ H^2\end{matrix}\right\} O^4 + 2\ aq.\right)$, bringing it to the type of normal plumbic acid $\left(\left.\begin{matrix}Pb^{iv}\\ H^4\end{matrix}\right\} O^4\right)$. Heated with an acid, plumbic anhydride leaves its oxygen and is transformed into a salt of lead; consequently a mixture of plumbic anhydride and sulphuric acid is a strong oxidant.

$$\underset{\text{Plumbic anhydride.}}{2\left(PbO^2\right)} + \underset{\text{Sulphuric acid.}}{2\left(\left.\begin{matrix}SO^{2\prime\prime}\\ H^2\end{matrix}\right\} O^2\right)} = \underset{\text{Sulphate of lead.}}{2\left(\left.\begin{matrix}SO^{2\prime\prime}\\ Pb^{\prime\prime}\end{matrix}\right\} O^2\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\ H\end{matrix}\right\} O\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\ O\end{matrix}\right\}}$$

**Minium or Saline Oxide** ($Pb^3O^4$).—This oxide may be regarded as a salt derived from the normal plumbic acid by the substitution of $Pb^{\prime\prime 2}$ for $H^4$.

$$\underset{\text{Plumbic acid.}}{\left(\left.\begin{matrix}Pb^{iv}\\ H^4\end{matrix}\right\} O^4\right)} - \underset{\text{Hydrogen.}}{2\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}\right)} + \underset{\text{Lead.}}{2Pb^{\prime\prime}} = \underset{\text{Plumbate of lead (minium).}}{\left(\left.\begin{matrix}Pb^{iv}\\ Pb^{\prime\prime 2}\end{matrix}\right\} O^4\right)}$$

Minium may be prepared by mixing the potassic solution of plumbic anhydride and protoxide of lead; the minium precipitates in a hydrated state.

In manufactures minium is obtained by the simultaneous action of air and heat on the protoxide; thus prepared its composition varies.

Minium is of a beautiful red colour; it is used in painting.

**Distinctive Characters of Salts of Lead.**—The soluble salts of lead are recognized by the following characters:

1st. Hydrochloric acid produces a white precipitate, which ammonia does not dissolve nor alter in colour. It dissolves in boiling water, and is deposited in crystalline scales on the cooling of the solution.

2nd. Hydrosulphuric acid causes the formation of a black precipitate of sulphide of lead, which is insoluble in the sulphide of ammonium, and is attacked by boiling nitric acid, which transforms part of it into soluble nitrate and part into insoluble sulphate.

3rd. Sulphuric acid precipitates these salts white. The precipitate dissolves in the tartrate of ammonium.

4th. With salts of lead, soluble chromates give a yellow precipitate, soluble in potash.

5th. Fixed alkalies give rise to a white precipitate, soluble in an excess of the reagent.

**Action of Lead on the Animal Economy.**—The compounds of lead exercise a deleterious action on the animal economy. Persons exposed to this action undergo morbid phenomena, which vary in intensity.

The first stage of poisoning is the painter's colic—violent pains in the intestines. The second consists in the extension of these pains into he limbs, and especially into the articulations (lead arthralgia). In he third stage paralysis of the limbs is produced, which is first

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manifested in the extensor muscles of the forehand. In some cases wasting of the brain with dementia occurs, which generally proves fatal.

In less serious cases the poisoning is treated by purgatives to facilitate the elimination of the poison, followed by tonics. The use of sulphuric acid in a diluted form is also advisable; and, as prophylactics, sulphur baths and great personal cleanliness are recommended to workers in lead.

## PLATINUM Pt.

Atomic weight = 197. Molecular weight unknown.

Until recently the metallurgic treatment of platinum was by means of solution. The ore was mechanically freed from any earthy matters it might contain, and then acted on by aqua regia which dissolved the platinum and a little iridium. The solution was then decanted, evaporated almost to dryness, and precipitated by a concentrated solution of chloride of ammonium. The precipitate of double chloride of ammonium and platinum thus produced was washed with diluted alcohol, and then calcined. There remained a spongy mass of platinum (spongy platinum), which was reduced to powder, and then made into a paste with water. This paste, when pressed in an iron cylinder, gave a compact metallic mass, which was then heated to redness, and aggregated by beating with a hammer at this high temperature.

In 1861 M. Deville published a very important work on the metallurgy of platinum, in which he substituted an entirely new method.

100 parts of ore, mechanically freed from its impurities, are melted with an equal weight of galena (sulphide of lead); the iron contained in the ore seizes the sulphur of the galena, and the platinum is alloyed with the liberated lead. 50 parts of lead are then added to the melted mass, and the heat continued, stirring until the action is complete; the temperature during this operation ought to be at least equal to the fusing point of gold, or even somewhat higher. When the process has thus far advanced, air is blown into the crucible, the sulphur passes to the state of sulphurous anhydride, which is disengaged; part of the galena passes to the state of lead, which unites with the platinum alloy; while the iron and copper, which were in the state of sulphide, form oxides on the surface. When sulphurous anhydride is no longer disengaged, two parts of binoxide of manganese and about ten parts of glass are added to the mixture, and a fusible scoria is formed containing manganese, iron, copper, and glass. The mass is then allowed to cool, the crucible is broken, and the alloy of platinum and lead, which is easily separated from the scoria, is extracted.

This alloy is then placed in a porous cupel made of burnt bone, which is itself placed over a crucible full of coke with a hole in its lower part; the crucible and cupel are then heated in contact with air in a special furnace, and the lead is oxidized and passes to the state of litharge. This melts, passes through the pores of the bone cupel, and falls on to the coke; there it is reduced, and metallic lead remains, which runs out through the lower part of the crucible. This operation (cupellation) gives crude platinum, which still contains small portions of lead, osmium, iridium, and rhodium. The metal is placed on a small bed of lime, and melted by means of the oxyhydrogen blowpipe, and kept melted until it disengages neither the vapour of lead nor the odour of osmium.

Platinum thus obtained contains iridium and rhodium, but this alloy is superior to pure platinum for most purposes, as it is harder and resists a higher temperature.

In this process about 10 kilogrammes of ore are usually operated on at once.

In order to obtain perfectly pure platinum, the platinum of commerce must be dissolved in aqua regia and lime added in the dark; the iridium is precipitated in the state of oxide; then the liquid must be filtered, and the platinum precipitated by means of chloride of ammonium. This precipitate is washed and calcined, and spongy platinum remains, which can be employed in this state to prepare the different platinum compounds.

Platinum can also be obtained in the form of a black powder (platinum black) by heating an alcoholic solution of potash with bichloride of platinum until effervescence ceases. The black powder which deposits ought to be washed, first with alcohol, next with hydrochloric acid, then with potash, and finally with water.

The aggregated platinum is of a bright white colour, but it is not so white as silver. Platinum ranks third in ductility and fifth in malleability; a platinum wire of two millimetres in diameter breaks under a weight of 124 kilogrammes.

Platinum is harder than silver, but not so hard as copper or iron; its density is from 21·15 to 21·47. It is found native crystallized in hexahedra, and is isomorphous in several of its compounds with iridium and osmium.

Platinum resists the highest heat of the forge, but it may be easily melted by the oxyhydrogen blowpipe: at red heat it can be welded like iron.

Platinum does not oxidize at any temperature; nitric acid does not attack it, unless it be alloyed with silver; aqua regia dissolves it, causing it to pass to the state of chloride. Potash and lithia cause the oxidation of platinum, and a fusible alkaline platinate is formed. This oxidation is especially rapid in presence of nitrate of potassium. Soda causes oxidation less readily than the other two alkalies.

Bisulphate of potassium also attacks platinum when hot, but bromine and iodine do not affect it; chlorine combines with it slowly. Phosphorus and arsenic combine with it when hot, forming a fusible phosphide and arsenide: when a phosphuretted organic matter is heated in a platinum crucible, the crucible is quickly pierced by the phosphorus set free.

Sulphur also can combine with platinum by the aid of heat if the metal be in the spongy state.

In presence of charcoal, silica transforms platinum into a fusible silicide; therefore a crucible of this metal ought never to be heated directly in a charcoal fire, or else the silica contained in the charcoal will destroy the crucible.

Finely-powdered platinum unites with mercury: this amalgam may be obtained by reducing a platinic compound by electricity in presence of mercury.

Platinum can act by catalysis even when it is laminated; but this property is manifested with the greatest intensity by spongy platinum and platinum black. We have already seen how spongy platinum determines the ignition of hydrogen, and in organic chemistry we shall see that platinum black is used to oxidize a number of substances.

Platinum is tetratomic; it forms two series of compounds, in one of which it only takes part with a value of substitution equal to two; in the other it acts with its maximum capacity for saturation. Thus there exist:

| | |
|---|---|
| A protochloride of platinum | $PtCl^2$ |
| A tetrachloride | $PtCl^4$ |
| A tetrabromide | $PtBr^4$ |
| A prot-iodide | $PtI^2$ |
| A tetr-iodide | $PtI^4$ |

The tetrachloride and tetrabromide of platinum can unite with the alkaline chlorides, bromides, and iodides, giving double chlorides, the formula of which is:

$$(PtCl^4, 2MCl).$$

The tetrachloride of platinum is obtained by dissolving the metal in aqua regia and evaporating to drive off the excess of acid. It readily dissolves in water, alcohol, and ether; it melts when heated, and if it be strongly heated, it decomposes first into chlorine and protochloride, and then into chlorine and platinum. The double salts it forms with alkaline chlorides are almost insoluble in water and quite insoluble in alcohol. At red heat they decompose into alkaline chloride, platinum, and chlorine. The double chloride of platinum and ammonium leaves a residue of platinum only, on account of the volatility of the chloride of ammonium.

There also exist two sulphides of platinum, a protosulphide (PtS), and a persulphide ($PtS^2$). They are obtained by double decomposition, by causing hydrosulphuric acid to act on the corresponding chlorides.

$$\underset{\text{Perchloride of platinum.}}{\left(PtCl^4\right)} + \underset{\text{Hydrosulphuric acid.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\} S\right)} = \underset{\text{Hydrochloric acid.}}{4\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Persulphide of platinum.}}{\left(PtS^2\right)}$$

These sulphides dissolve in alkaline sulphides, and in consequence act as acid anhydro-sulphides.

Two oxides of platinum, corresponding to the two sulphides, are known; the protoxide ($PtO$) and the peroxide ($PtO^2$). The first is obtained by the action of potash on the protochloride, and the second by the action of the same alkali on the tetrachloride; but these oxides being soluble in alkalies, the solution ought afterwards to be precipitated by an acid. A hydrate corresponds to each of these oxides; that answering to the protoxide (the protohydrate) has not been analyzed; its probable formula is $\left(\begin{matrix}Pt'' \\ H^2\end{matrix}\right\} O^2\Big)$; the formula of the perhydrate corresponding to the peroxide is $\left(\begin{matrix}Pt^{iv} \\ H^4\end{matrix}\right\} O^4\Big)$.

The typical hydrogen of these hydrates can be replaced either by acid radicles, in which case salts of platinum are formed, or by alkaline metals, when platinates are formed. These hydrates are therefore both acids and bases, and their anhydrides ought to be considered as indifferent oxides.

**Reactions of Salts of Platinum.**—The salts of platinum are recognized by the following characters:

1st. Hydrochloric acid does not precipitate them.

2nd. Hydrosulphuric acid forms a precipitate soluble in the alkaline sulphides, and insoluble in hydrochloric or nitric acids employed separately, but soluble in aqua regia.

3rd. In their solutions when not too dilute, the chloride of ammonium and the chloride of potassium form yellow precipitates; even with dilute solutions the precipitate is formed if a little alcohol be added.

## GENERAL REMARKS ON THE TETRATOMIC METALS.

We have seen that this class contains all bodies the atomicity of which is somewhat doubtful. The following questions may be asked:

1st. Why not make iron, aluminium, manganese, nickel, cobalt, and chromium hexatomic, resting on the existence of the fluoride of chromium ($CrFl^6$)?

2nd. Why not follow in regard to zinc, cadmium, magnesium, calcium, strontium, barium, copper, mercury, etc., the same reasoning as in regard to nickel, and not consider their real atomicity as equal to 4, their apparent atomicity being only 2? Could not the isomorphism of their compounds with those of nickel, cobalt, iron (*ad minimum*), etc., be used in favour of this opinion?

3rd. Why should we not consider platinum and palladium as having a real atomicity equal to 6, basing our opinion on the incontestable analogies of platinum and palladium, and on the isomorphism of the compounds of platinum with those of iridium? I will successively answer these three questions.

1st. I do not take the fluoride of chromium ($CrFl^6$) into account, because its formula does not appear to me to be established.

2nd. I cannot consider magnesium, zinc, etc., as tetratomic. In fact, mercury not forming part of the magnesian series, nothing can make its atomicity 4. But copper has such analogies with mercury that these two metals must be allowed to have similar atomicities; and the isomorphism of the other magnesian metals with copper, leads us to call these metals biatomic, just as their isomorphism with iron and nickel leads us to consider them as tetratomic. It is possible that some of them ought to be considered nearer nickel than copper, but we have no means of knowing this, and therefore are obliged to keep to the apparent atomicity.

Moreover, the isomorphism of two given compounds is not conclusive as to the presumable existence of compounds of an order higher than those acknowledged to be isomorphous. Thus, it would not be correct to say: salts of zinc are isomorphous with proto-salts of iron, per-salts of iron exist, therefore per-salts of zinc must exist, or at least, if these salts are unstable, the atomicity of zinc, like that of iron, is 4.

M. Marignac has shown that two bodies are isomorphous when they contain the same number of simple atoms similarly arranged, whatever may be the atomicity of these latter. Thus he has shown that two compounds containing the same number of atoms are isomorphous, though one may contain fluorine and the other oxygen.

Therefore, it may easily be conceived that the protosulphate of iron $\left(\left.\begin{matrix}SO^{2\prime\prime}\\ Fe^{\prime\prime}\end{matrix}\right\} O^2 + 7\text{ aq.}\right)$ and the sulphate of zinc $\left(\left.\begin{matrix}SO^{2\prime\prime}\\ Zn^{\prime\prime}\end{matrix}\right\} O^2 + 7\text{ aq.}\right)$ are isomorphous, because they contain the same number of simple atoms, without being obliged to allow the same atomicity for zinc as for iron.

3rd. The preceding considerations on isomorphism also answer the question relative to the atomicity of platinum. Certain compounds of this metal may be isomorphous with compounds of the same degree formed by iridium, without the atomicity of platinum being equal to 6. Nevertheless, I should not be surprised if some day new facts were discovered which would oblige us to admit the hexatomicity of platinum.

## FIFTH CLASS (PENTATOMIC METALS).

Up to the present time this class does not contain any metal.

## SIXTH CLASS (HEXATOMIC METALS).

We have seen that molybdenum, tungsten, iridium, rhodium, and ruthenium are arranged in this class. None of these metals possess sufficient interest for a detailed description to be given of them.

## GENERAL REMARKS ON THE OXIDES.

**Preparation.**—1st. When the body to be oxidized possesses the property of combining directly with atmospheric oxygen, as is the case with sulphur, phosphorus, zinc, iron, potassium, etc., the oxide is prepared by the direct combustion of the body in air.

2nd. When the body to be oxidized does not combine directly with oxygen, it is heated in presence of oxidizing agents, such as nitric acid, and then either a hydrate is produced, if the oxide to be prepared is an acid anhydride like the oxide of tin; or if the oxide be a basic anhydride like the greater part of the metallic oxides, a nitrate is produced. On calcining the hydrate or nitrate, an anhydrous oxide is obtained.

3rd. The carbonate of the metal of which the oxide is to be obtained is calcined, carbonic anhydride is disengaged, and the oxide remains as a residue. The alkaline carbonates and those of barium and strontium alone cannot be decomposed by heat.

4th. A chloride or any other soluble salt is precipitated by an alkaline base, and there remains either a precipitate of oxide, as takes place with the salts of silver, which is collected and washed; or else a precipitate of hydrate, which must be washed and calcined to bring it to the state of anhydrous oxide.

5th. A peroxide is heated in a current of hydrogen gas to reduce it to a lower state of oxidation. Protoxide of manganese is thus prepared from the peroxide.

6th. Certain peroxides are obtained by the action of oxygenated water on the protoxides.

**Classification.**—Oxides have been arranged in five classes:

1st. In the first are placed the basic oxides, or, according to the proper expression, the *basic anhydrides.*

2nd. In the second we find the acid oxides, or, to use a better term, the *acid anhydrides.*

3rd. The third contains the oxides acting sometimes as acid anhydrides, and sometimes as basic anhydrides: they are called *indifferent oxides.*

4th. The fourth class contains the oxides that may be considered as rue salts, in which a part of the metal appears to be substituted for he hydrogen of a hydrate of the same body, acting as an acid; such is he magnetic oxide of iron ($Fe^3O^4$), which may be regarded as resulting rom the substitution of one atom of iron for two of hydrogen in the ydrate $\left.\begin{matrix}Fe^2\\H^2\end{matrix}\right\}O^4$. These are called *saline oxides.*

5th. In the fifth class, chemists place those oxides which are neither asic anhydrides nor acid anhydrides, but which can be transformed nto basic anhydrides by the loss of a portion of their oxygen, and ometimes into acid anhydrides by the addition of another quantity of xygen: these may be called *peculiar oxides.*

A sixth class ought to be added to these, which should contain all the oxides that cannot be classed in any of the preceding. Among the number of these would be the oxide of carbon, the protoxide and binoxide of nitrogen, etc.

**Action of Different Agents on the Oxides.**—1st. ACTION OF HEAT.—With the exception of the oxides of platinum, rhodium, iridium, palladium, ruthenium, and mercury, which can be decomposed by heat alone, the metallic protoxides resist the highest temperatures that can be produced. The higher oxides are often reduced to a lower degree of oxidation.

Among the oxides of the metalloids, some resist the action of heat, while others are decomposed. Water is decomposed at 2500° under the influence of heat alone.

2nd. ACTION OF LIGHT.—Certain oxides, fixed in the tissues, are modified under the influence of light, without our being able to determine in what the modification they undergo consists.

3rd. ACTION OF ELECTRICITY.—The electric current, when sufficiently powerful, decomposes the oxides. Sometimes the products of the decomposition are the two elements of the oxide, as is seen in the electrolysis of water; sometimes these products are oxygen and an oxide that is less oxygenated than the first, as in the case of carbonic anhydride, which is transformed into oxide of carbon and oxygen.

As the metallic oxides are mostly insoluble in water, and as those which can be dissolved pass to the state of hydrates, the action of electricity on these bodies has not as yet been tried. It might perhaps be tried on those that are fusible by maintaining them at the point of fusion during the passage of the current. It cannot, however, be doubted that electricity would decompose them as it decomposes the most stable hydrates.

4th. ACTION OF OXYGEN.—Oxygen is either without action on the oxides, or it causes them to pass to a higher state of oxidation. An example of the latter mode of action occurs in the transformation of the protoxide of barium into binoxide of the same metal, and in the combustion of the oxide of carbon.

5th. ACTION OF HYDROGEN.—Hydrogen has absolutely no action on the protoxides of alkaline metals, alkaline earths or earths. Under the influence of a gentle heat, it reduces the protoxides of most of the other metals, liberating the metal. The protoxide of manganese, however, resists its action.

In acting on the peroxides of the metals whose protoxides are not affected by it, hydrogen reduces these bodies to the minimum of oxidation. Thus by means of a current of hydrogen the binoxide of manganese is transformed into protoxide.

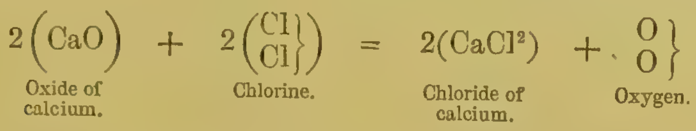
Certain highly-oxygenated oxides, such as the sesquioxide of chromium, resist the action of hydrogen.

6th. ACTION OF CARBON.—Carbon has a reducing action still more powerful than that of hydrogen; it seizes the oxygen of oxides to form either carbonic anhydride or oxide of carbon; and the radicle of these oxides remains either in a free state or in a lower state of oxidation.

7th. Action of Chlorine.—Chlorine has very little action on the oxides of metalloids; at the most it only combines with some of them which are not saturated. On acting on these latter in presence of water, it can also cause them to pass to a higher state of oxidation.

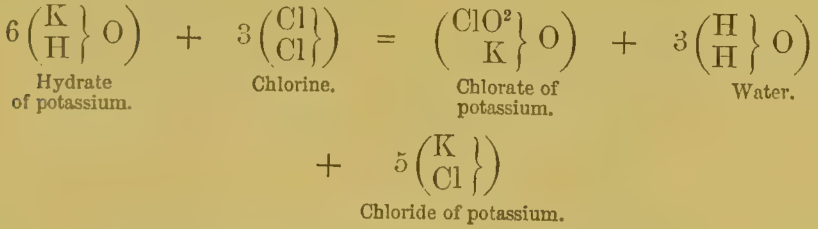
Chlorine acts differently on metallic oxides, according as the action takes place in presence of moisture or not.

Chlorine, when dry, displaces oxygen, and a chloride is formed:



$$\underset{\text{Oxide of calcium.}}{2\left(\text{CaO}\right)} + \underset{\text{Chlorine.}}{2\left(\begin{matrix}\text{Cl}\\ \text{Cl}\end{matrix}\right\}\Big)} = \underset{\text{Chloride of calcium.}}{2(\text{CaCl}^2)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}\text{O}\\ \text{O}\end{matrix}\right\}}$$

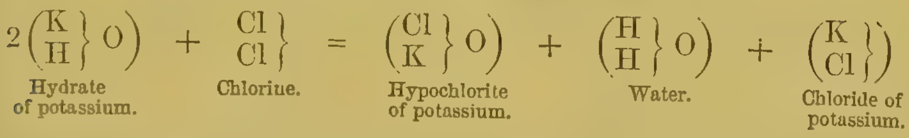
In presence of water several cases may occur; sometimes a mixture of chloride and chlorate is formed:



$$\underset{\text{Hydrate of potassium.}}{6\left(\left.\begin{matrix}\text{K}\\ \text{H}\end{matrix}\right\}\text{O}\right)} + \underset{\text{Chlorine.}}{3\left(\left.\begin{matrix}\text{Cl}\\ \text{Cl}\end{matrix}\right\}\right)} = \underset{\text{Chlorate of potassium.}}{\left(\left.\begin{matrix}\text{ClO}^2\\ \text{K}\end{matrix}\right\}\text{O}\right)} + \underset{\text{Water.}}{3\left(\left.\begin{matrix}\text{H}\\ \text{H}\end{matrix}\right\}\text{O}\right)}$$

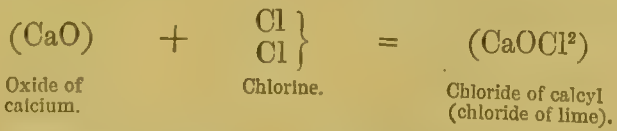
$$+ \underset{\text{Chloride of potassium.}}{5\left(\left.\begin{matrix}\text{K}\\ \text{Cl}\end{matrix}\right\}\right)}$$

sometimes a mixture of chloride and hypochlorite:



$$\underset{\text{Hydrate of potassium.}}{2\left(\left.\begin{matrix}\text{K}\\ \text{H}\end{matrix}\right\}\text{O}\right)} + \underset{\text{Chlorine.}}{\left.\begin{matrix}\text{Cl}\\ \text{Cl}\end{matrix}\right\}} = \underset{\text{Hypochlorite of potassium.}}{\left(\left.\begin{matrix}\text{Cl}\\ \text{K}\end{matrix}\right\}\text{O}\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}\text{H}\\ \text{H}\end{matrix}\right\}\text{O}\right)} + \underset{\text{Chloride of potassium.}}{\left(\left.\begin{matrix}\text{K}\\ \text{Cl}\end{matrix}\right\}\right)}$$

Sometimes the chlorine is simply added to the oxide, forming an unstable compound, which is destroyed by all acids with liberation of the chlorine.



$$\underset{\text{Oxide of calcium.}}{(\text{CaO})} + \underset{\text{Chlorine.}}{\left.\begin{matrix}\text{Cl}\\ \text{Cl}\end{matrix}\right\}} = \underset{\text{Chloride of calcyl (chloride of lime).}}{(\text{CaOCl}^2)}$$

The action of bromine and iodine is precisely similar to that of chlorine.

8th. Action of Sulphur.—The oxides of metalloids contain a radicle that is either more or less easily oxidized than sulphur. In the first case the sulphur seizes the whole, or at least a portion of the oxygen of the oxide, which is reduced. In the second case the sulphur produces no reaction whatever.

When sulphur is made to react on basic oxides the affinity of sulphur for the metal causes the decomposition of a part of the oxide, and a metallic sulphide is formed. A second part of the sulphur unites with the oxygen the oxide has lost. Thus a certain quantity of an acid anhydride is produced, which, on reacting on a portion of the undecomposed basic anhydride, furnishes an oxygenated salt of sulphur. When the operation is performed with dry materials and under the influence of heat, if the oxygenated salts of sulphur which tend to be formed are stable, they are effectively formed; if they are instable, all the oxygen is eliminated in the state of sulphurous anhydride, and the whole of the metal remains in the state of sulphide. Finally, if the metallic sulphide be itself instable at the temperature at which the reaction takes place, only sulphurous anhydride and free metal are produced. These three kinds of reactions are expressed by the following equations:

$$\text{1st.}\quad \underset{\text{Baryta.}}{4(\text{BaO})} + \underset{\text{Sulphur.}}{2\left(\left.\begin{matrix}\text{S}\\\text{S}\end{matrix}\right\}\right)} = \underset{\text{Sulphide of barium.}}{3(\text{BaS})} + \underset{\text{Sulphate of barium.}}{(\text{SBaO}^4)}$$

$$\text{2nd.}\quad \underset{\text{Oxide of copper.}}{2(\text{CuO})} + \underset{\text{Sulphur.}}{\left.\begin{matrix}\text{S}\\\text{S}\end{matrix}\right\}} = \underset{\text{Subsulphide of copper.}}{(\text{Cu}^2\text{S})} + \underset{\text{Sulphurous anhydride.}}{(\text{SO}^2)}$$

$$\text{3rd.}\quad \underset{\text{Peroxide of platinum.}}{2(\text{PtO}^2)} + \underset{\text{Sulphur.}}{\left.\begin{matrix}\text{S}\\\text{S}\end{matrix}\right\}} = \underset{\text{Platinum.}}{2\text{Pt}} + \underset{\text{Sulphurous anhydride.}}{2(\text{SO}^2)}$$

When the operation is conducted in the presence of moisture, there is formed a sulphide and an oxygenated salt of sulphur, as in the first reaction, but instead of a sulphate, a hyposulphite is formed:

$$\underset{\text{Hydrated oxide of barium.}}{3\left(\left.\begin{matrix}\text{Ba}''\\\text{H}^2\end{matrix}\right\}\text{O}^2\right)} + \underset{\text{Sulphur.}}{2\left(\left.\begin{matrix}\text{S}\\\text{S}\end{matrix}\right\}\right)} = \underset{\text{Sulphide of barium.}}{2\left(\text{Ba}''\text{S}\right)} + \underset{\text{Water.}}{3\left(\left.\begin{matrix}\text{H}\\\text{H}\end{matrix}\right\}\text{O}\right)} + \underset{\text{Hyposulphite of barium.}}{\left(\text{S}^2\text{BaO}^3\right)}$$

Selenium and tellurium present a complete parallelism with sulphur in their reactions on the oxides.

9th. Action of Phosphorus.—The action of phosphorus is analogous to that of sulphur. Phosphorus seizes the oxygen of the unstable oxides of the metalloids, and does not react on those which present a certain stability. It decomposes metallic oxides, forming a phosphide and an oxygenated salt. When the operation is conducted in the dry way, this oxygenated salt is always a phosphate; by the moist way, a hypophosphite is produced, and phosphuretted hydrogen is disengaged. The formation of a phosphide is no longer observed here, because these bodies are decomposed by water.

With the exception of nitrogen, which has no action on the oxides, the congeners of phosphorus appear to act in the same way as phosphorus itself.

10th. Action of Metals.—The metallic oxides are decomposed by metals that are more electro-positive than those they contain: a simple displacement is then produced:

$$\underset{\text{Metallic oxide.}}{(MO)} + \underset{\text{More positive metal.}}{M'} = \underset{\text{Oxide of more positive metal.}}{(M'O)} + \underset{\text{Metal (less positive).}}{M}$$

The oxides of metalloids are decomposed in an analogous manner by metals, only the metallic oxide formed unites with a portion of the negative oxide that has remained intact, and an oxygenated salt of the metal is produced.

11th. Action of Water.—Directly or indirectly, most of the oxides are capable of entering into combination with water, or of giving rise to the phenomenon of double decomposition. Bodies are then produced which have received the name of hydrates. These hydrates represent a molecule of water or several molecules of water condensed into one, in which a part of the hydrogen is replaced by another radicle. In anhydrous oxides, on the contrary, the hydrogen is wholly replaced:

$$\underset{\text{Hydrate of potassium.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} \qquad \underset{\text{Anhydrous oxide of potassium.}}{\left(\left.\begin{matrix}K\\K\end{matrix}\right\}O\right)}$$

$$\underset{\text{Hydrate of calcium.}}{\left(\left.\begin{matrix}Ca''\\H^2\end{matrix}\right\}O^2\right)} \qquad \underset{\text{Anhydrous oxide of calcium.}}{\left(Ca''O\right)}$$

Certain peculiar oxides of metals, the protoxides of which under the influence of water give very stable hydrates, are decomposed by hat liquid, and brought to the minimum of oxidation. This is the ase with the peroxides of potassium and sodium.

Certain non-saturated oxides can decompose water, seizing its oxygen.

All oxides are insoluble in water, with the exception of alkaline xides and alkaline earths.

12th. Action of Bases.—Bases do not act on basic anhydrides; with cid anhydrides they give rise to salts, setting free water:

$$\underset{\text{Hydrate of potassium.}}{2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} + \underset{\text{Sulphuric anhydride.}}{(SO^3)} = \underset{\text{Potassic sulphate.}}{(SK^2O^4)} + \underset{\text{Water.}}{(H^2O)}$$

13th. Action of Acids.—Acids have no action on acid anhydrides. n presence of basic anhydrides they form salts, liberating water.

$$\underset{\text{Nitric acid.}}{2\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)} + \underset{\text{Anhydrous oxide of potassium.}}{\left(\left.\begin{matrix}K\\K\end{matrix}\right\}O\right)} = \underset{\text{Nitrate of potassium.}}{2\left(\left.\begin{matrix}NO^2\\K\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

The different species of salts resulting from the action of acid anhyides on water or on bases deserve to be studied separately.

**Nitrates.**—Nitrates are obtained by dissolving metallic oxides or rbonates in nitric acid. All are decomposed by heat, leaving as a residue either a metallic oxide, or a metal in a free state if the oxide be instable when hot. Alkaline nitrates leave a residue of nitrite when moderately calcined. All neutral nitrates are soluble in water.

The nitrates deflagrate on red-hot coals. Heated with sulphuric acid, they disengage vapours having the odour of nitric acid; if copper be added to the mixture, binoxide of nitrogen is produced, which on contact with air is transformed into red vapours of hyponitride.

If a nitrate in solution be mixed with a solution of protosulphate of iron strongly acidulated with sulphuric acid, a colour is produced which varies from rose to brown, according to the concentration of the nitrate.

With soluble nitrates, the sub-acetate of lead in aqueous solution gives a white precipitate of sub-nitrate of lead answering to the formula $\left.\begin{matrix} Pb'' \\ (NO^2) \\ H \end{matrix}\right\} O^2$. It is very slightly soluble in water.

**Nitrites.**—Nitrites are obtained by moderately heating nitrates.

It is not known whether with the sub-acetate of lead nitrites give a sub-nitrite of lead like the nitrates.

These salts also possess the property of deflagrating on burning coals.

With sulphuric acid they give rise to a development of red vapours, without its being necessary to add copper to the mixture.

Heated with a solution of sal-ammoniac, they disengage nitrogen, which arises from the decomposition of the nitrite of ammonium which is first formed.

Neutral nitrites are all soluble in water.

**Phosphates.**—With the exception of the alkaline phosphates, all neutral phosphates are insoluble. Acid phosphates, on the contrary, readily dissolve.

With the nitrate of barium, the solutions of phosphates give a white precipitate soluble in water acidulated with nitric or hydrochloric acid.

The salts of lead produce a white precipitate of phosphate of lead.

Nitrate of silver gives a clear yellow precipitate, soluble in ammonia and in dilute nitric acid.

Salts of copper give a dirty-blue precipitate.

The phosphates give a granulated precipitate with the soluble ammonio-magnesian double salts.

When a phosphate is heated with a solution of molybdate of ammonium acidulated with nitric acid, a yellow precipitate is produced. This reaction is very perceptible.

**Phosphites.**—The soluble phosphites are obtained by saturating phosphorous acid by bases, and the other phosphites by double decomposition.

Alkaline phosphites alone are soluble in water. The solutions of phosphites reduce certain metallic oxides, especially in presence of hydrochloric acid. The red mercuric oxide, for instance, is thus reduced to the metallic state. Phosphites disengage phosphuretted hydrogen when calcined, and are transformed into phosphates.

Nitric acid and chlorine cause the same transformation. When heated with a solution of molybdate of ammonium in hydrochloric acid, phosphites give a blue colour resulting from the reduction of the molybdic acid.

**Hypophosphites.**—Hypophosphites are obtained by heating phosphorus with a powerful base in presence of water.

They all decompose by heat, leaving a residue of phosphate. Nitric acid and chlorine produce the same transformation.

The hypophosphites also reduce the salts of palladium, causing a deposit of metallic palladium.

The same reaction takes place with salts of silver. The liquid from which the metal is separated contains a phosphate in solution.

**Arseniates.**—Alkaline arseniates only are soluble in water. The salts of barium, with soluble arseniates, give a white precipitate of arseniate of barium, which is soluble in acidulated water and in the solution of hydrochlorate of ammonia.

Sulphuretted hydrogen transforms arseniates into sulpho-arseniates. On saturating the liquid afterwards with hydrochloric acid, a yellow precipitate of sulphide of arsenic is obtained, which is soluble in alkaline sulphides and in ammonia. With free arsenic acid, hydrosulphuric acid gives this precipitate direct, but it requires a long time to form.

With soluble arseniates, nitrate of silver gives a brick-red precipitate of arseniate of silver.

Salts of copper cause the formation of a dirty-blue precipitate.

When introduced into Marsh's apparatus, arseniates give rise to arseniuretted hydrogen, by the combustion of which specks of arsenic can be collected.

**Arsenites.**—Alkaline arsenites only are soluble in water. Solutions of arsenites slightly acidulated with hydrochloric acid give, under the influence of sulphuretted hydrogen, a yellow precipitate of the trisulphide of arsenic, which is insoluble in acids and soluble in alkaline sulphides and in ammonia.

In solutions of the arsenites, salts of barium produce a white precipitate, soluble in hydrochloric acid and in chloride of ammonium.

The salts of copper give a precipitate of arsenite of copper of a beautiful green colour.

Nitrate of silver gives rise to a clear yellow precipitate of arsenite of silver.

When introduced into Marsh's apparatus, arsenites give rise to the same reaction as arseniates.

**Sulphates.**—Soluble sulphates are obtained by saturating sulphuric acid with bases, and insoluble sulphates by double decomposition.

All the neutral sulphates are soluble with the exception of those of barium, strontium, and lead, which are quite insoluble, and sulphate of calcium, which requires about 500 parts of water to dissolve it. Therefore sulphates in solution in water give a white precipitate with the salts of calcium, barium, strontium, and lead; if the solution be greatly diluted, the salts of calcium will not be precipitated.

Heated with charcoal, the sulphates are transformed into sulphides, and consequently acquire the property of diffusing the odour of hydrosulphuric acid under the influence of acids.

Some sulphates decompose by boiling, and leave a subsulphate which is insoluble in water. The sulphate of mercury is of this number.

**Sulphites.**—Soluble sulphites may be prepared by transmitting a current of sulphurous anhydride into water holding a base in solution or in suspension. The other sulphites are obtained by double decomposition.

Soluble sulphites and the solution of sulphurous anhydride give, in presence of salts of barium, a white precipitate that is soluble in dilute acid. This solution, when exposed to the action of chlorine, deposits the sulphate of barium.

When a sulphite is heated with an acid which is relatively fixed and which has no oxidizing action, sulphurous anhydride is disengaged. This body may be easily recognized by its odour and the property it possesses of turning blue a starch paper moistened with a solution of iodic acid.

With nitrate of silver, the soluble sulphites give an abundant white precipitate, soluble in ammonia.

**Hyposulphates (dithionates).** — The different hyposulphates are prepared by precipitating the hyposulphate of barium by soluble sulphates.

Hyposulphates are not oxidized when cold, either by chlorine or by the binoxide of manganese; at boiling point this oxide causes them to pass to the state of sulphates.

When a hyposulphate is calcined, sulphurous anhydride is disengaged, and a sulphate remains as residue.

**Hyposulphites.**—Hyposulphites are obtained by boiling the sulphites with a quantity of sulphur equal to that they already contain.

A solution of a salt of silver added to that of a hyposulphite produces a white precipitate, which becomes black on changing into sulphide. This transformation is produced very rapidly by heat.

The hyposulphites treated by a strong acid give rise to a disengagement of sulphurous anhydride and to a deposit of sulphur.

The hyposulphites readily dissolve the chloride, bromide, iodide, and cyanide of silver.

**Chlorates.** — Chlorates are all soluble in water; they deflagrate strongly when thrown on to hot coals. When mixed with combustible bodies, like sulphur or charcoal, they detonate by heat.

Alkaline chlorates, submitted to the influence of heat, lose oxygen and leave a residue of chloride; the others lose both chlorine and oxygen, and leave an oxychloride as residue.

Treated by sulphuric acid, chlorates give rise to a yellow gas which is very explosive; it is improperly called hypochloric acid.

**Perchlorates.**—The different perchlorates are obtained by dissolving bases in perchloric acid.

The perchlorate of potassium being very little soluble in the cold, a crystalline precipitate is formed whenever a solution of a salt of potash is mixed with perchloric acid.

Sulphurous anhydride and hydrosulphuric acid have no action on perchloric acid or the perchlorates.

When strongly calcined, the perchlorates lose their oxygen and leave a residue of chloride.

**Hypochlorites.**—Hypochlorites and hypochlorous anhydride possess the property of bleaching organic substances, but they lose it when mixed with a solution of arsenious anhydride in nitric acid.

Carbonic anhydride in excess disengages hypochlorous anhydride from the hypochlorites, though the solution of hypochlorous anhydride decomposes the carbonates with effervescence.

**Chlorites.**—Chlorous anhydride is a yellow gas, which colours water very strongly, dissolving in this liquid.

Chlorous anhydride and chlorites bleach organic substances, and retain this property in presence of a solution of arsenious anhydride in nitric acid.

Chlorites disengage chlorous anhydride under the influence of a strong current of carbonic anhydride.

**Borates.**—The soluble borates are prepared by causing boracic acid to act on bases, and the insoluble borates by double decomposition.

Soluble salts of barium give, with borates, a precipitate of borate of barium, soluble in dilute hydrochloric acid and in the solution of hydrochlorate of ammonia.

The alkaline borates give an aqueous solution which, when saturated, is precipitated by acids when cold. The precipitate which forms is boracic acid and is dissolved on boiling the liquid. When a borate is mixed with sulphuric acid and alcohol, and the alcohol is ignited, this latter burns with a beautiful green flame.

**Carbonates.**—With the exception of the alkaline carbonates, all carbonates are insoluble and may be obtained by means of double decomposition.

Carbonates readily decompose under the influence of heat; carbonic anhydride is disengaged and an oxide, or if this be unstable a residue of free metal remains. The alkaline carbonates, and those of barium and strontium, are the only exceptions.

Soluble carbonates give, with salts of barium, a white precipitate which is soluble in dilute acids.

In presence of acids, carbonates give rise to a disengagement of carbonic anhydride which precipitates lime-water white.

**Silicates.**—The alkaline silicates with a great excess of base are alone soluble in water.

Salts of barium produce in their solutions a white precipitate of silicate of barium which is soluble in hydrochloric acid. If potassic sulphate be added to the solution so as to eliminate the barium, and the liquid be filtered, it will give, with ammonia, a precipitate of gelatinous silica.

When hydrochloric acid is added to the solution of a silicate, a precipitate of gelatinous silica is produced, which is soluble in an excess of acid, but which can be easily separated by evaporating to dryness and redissolving in water. A similar precipitate, but which is insoluble in an excess of the reagent, is obtained when hydrochloric acid is replaced by the chloride of ammonium.

**Chromates.**—Chromates (neutral chromates) are yellow; the bichromates (or acid chromates) are red or orange-coloured. Both have considerable colouring power.

With metallic solutions, soluble chromates give precipitates many of which possess brilliant colours; among these is the precipitate furnished by the salts of lead, which is a beautiful yellow.

Heated with hydrochloric acid in presence of alcohol or of any other reducing agent, these salts become green, and a hydrated perchloride of chromium is formed.

Mixed with melted sea salt and sulphuric acid, the chromates form a mixture which, when distilled, furnishes a reddish liquid; and when this is decomposed by a solution of ammonia it becomes yellow, and then gives a precipitate with acetate of lead.

## GENERAL REMARKS ON SULPHIDES.

Sulphides present the strictest analogies to oxides, both in their properties and in their actions.

**Preparation.**—1st. Like oxides, many sulphides may be obtained by the direct union of sulphur with another body. Thus carbon, arsenic, copper, and iron, combine with sulphur with great avidity. But zinc, which unites so readily with oxygen, has only a very weak affinity for sulphur.

2nd. Certain sulphides which contain several atoms of sulphur are prepared by combining directly with this metalloid sulphides less sulphuretted than those to be obtained; thus the tersulphide of arsenic ($As^2S^3$) may be produced by heating the bisulphide ($As^2S^2$) with sulphur.

3rd. Sulphides may also be obtained by causing hydrosulphuric acid to act on certain soluble hydrates. In this case the sulphur of the hydrosulphuric acid and the oxygen of the hydrate are interchanged; a compound is first formed which represents hydrosulphuric acid, the half of the hydrogen of which is replaced by a radicle, and which is called a hydrosulphate; afterwards, on adding to the hydrosulphate an additional quantity of the primitive hydrate, water and a sulphide are formed:

$$(1)\quad \underset{\text{Hydrate of potassium.}}{\Bigl(\begin{matrix}K\\H\end{matrix}\Bigr\}O\Bigr)} + \underset{\text{Hydrosulphuric acid.}}{\Bigl(\begin{matrix}H\\H\end{matrix}\Bigr\}S\Bigr)} = \underset{\text{Water.}}{\Bigl(\begin{matrix}H\\H\end{matrix}\Bigr\}O\Bigr)} + \underset{\text{Hydrosulphate of potassium.}}{\Bigl(\begin{matrix}K\\H\end{matrix}\Bigr\}S\Bigr)}$$

$$(2)\quad \underset{\text{Hydrosulphate of potassium.}}{\Bigl(\begin{matrix}K\\H\end{matrix}\Bigr\}S\Bigr)} + \underset{\text{Hydrate of potassium.}}{\Bigl(\begin{matrix}K\\H\end{matrix}\Bigr\}O\Bigr)} = \underset{\text{Water.}}{\Bigl(\begin{matrix}H\\H\end{matrix}\Bigr\}O\Bigr)} + \underset{\text{Monosulphide of potassium.}}{\Bigl(\begin{matrix}K\\K\end{matrix}\Bigr\}S\Bigr)}$$

4th. By causing hydrosulphuric acid to act on a chloride.

$$\text{Ex.:}\quad \underset{\text{Perchloride of tin.}}{(SnCl^4)} + \underset{\text{Hydrosulphuric acid.}}{2\Bigl(\begin{matrix}H\\H\end{matrix}\Bigr\}S\Bigr)} = \underset{\text{Hydrochloric acid.}}{4\Bigl(\begin{matrix}H\\Cl\end{matrix}\Bigr\}\Bigr)} + \underset{\text{Bisulphide of tin.}}{(SnS^2)}$$

5th. By heating a sulphate with charcoal, which seizes the oxygen of the sulphate, and a sulphide remains as residue.

$$\text{Ex.:}\quad \underset{\text{Sulphate of barium.}}{(SBaO^4)} + \underset{\text{Carbon.}}{2\,C} = \underset{\text{Carbonic anhydride.}}{2\,(CO^2)} + \underset{\text{Sulphide of barium.}}{(BaS)}$$

**Classification.**—Among sulphides, some act as acids and others as basic anhydrosulphides; others, again, appear to be the mixed anhydrosulphides of two hydrosulphates derived from one simple body and acting, the one as sulpho-base, and the other as sulpho-acid; these are the saline sulphides. Sulphides are also known which act sometimes as acid and sometimes as basic anhydrosulphide; these are the indifferent sulphides.

There also exist sulphides containing more than one atom of sulphur for two electro-positive atoms of uneven atomicity, or for one of even atomicity; these are called polysulphides. They readily part with a portion of their sulphur, and may be considered as peculiar sulphides, corresponding to the peculiar oxides. There are therefore five classes of sulphides, corresponding to the five classes of oxides:

1st. The basic sulphides, corresponding to the basic oxides.

2nd. The acid sulphides, corresponding to the acid oxides.

3rd. The indifferent sulphides, corresponding to the indifferent oxides.

4th. The saline sulphides, corresponding to the saline oxides.

5th. The peculiar sulphides, corresponding to the peculiar oxides.

All the sulphides in question may be considered as derived from simple or condensed hydrosulphuric acid, in which the hydrogen is replaced either by a simple body or by a sulphuretted radicle; thus the sulphide of potassium is written $\Bigl(\begin{matrix}K\\K\end{matrix}\Bigr\}S\Bigr)$, the sulphide of barium $(Ba''S)$, the bisulphide of barium $(BaS''S)$, etc. There also exist, as we have already seen, other compounds which represent hydrosulphuric acid with only half of its hydrogen replaced by a simple body or by a sulphuretted radicle, which compounds have received the name of hydrosulphates. They correspond to the hydrates, and, like these latter, sometimes form bases, sometimes acids:

$$\begin{array}{cc}
\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right) & \left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{S}\right)\\
\text{Hydrate of potassium.} & \text{Hydrosulphate of potassium.}\\
\left(\left.\begin{matrix}\mathrm{CO}''\\ \mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right) & \left(\left.\begin{matrix}\mathrm{CS}''\\ \mathrm{H}^2\end{matrix}\right\}\mathrm{S}^2\right)\\
\begin{array}{c}\text{An unknown carbonic acid}\\ \text{(hydrate of carbonyl).}\end{array} & \begin{array}{c}\text{Sulphocarbonic acid}\\ \text{(hydrosulphate of sulphocarbonyl).}\end{array}
\end{array}$$

Metallic sulphides present reactions which enable them to be easily recognized, and even distinguish a monosulphide from a polysulphide and from a hydrosulphate.

All the metallic monosulphides, whether soluble or not, disengage hydrosulphuric acid under the influence of acids without the slightest deposit of sulphur being produced:

$$\begin{array}{ccccccc}
\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{K}\end{matrix}\right\}\mathrm{S}\right) & + & \left(\left.\begin{matrix}\mathrm{SO}^{2\prime\prime}\\ \mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right) & = & \left(\left.\begin{matrix}\mathrm{SO}^{2\prime\prime}\\ \mathrm{K}^2\end{matrix}\right\}\mathrm{O}^2\right) & + & \left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{S}\right)\\
\begin{array}{c}\text{Monosulphide}\\ \text{of potassium.}\end{array} & & \text{Sulphuric acid.} & & \begin{array}{c}\text{Sulphate of}\\ \text{potassium.}\end{array} & & \begin{array}{c}\text{Hydrosulphuric}\\ \text{acid.}\end{array}
\end{array}$$

When they are soluble, monosulphides, with the neutral chloride of manganese, give a flesh-coloured precipitate of sulphide of manganese without disengagement of hydrosulphuric acid:

$$\begin{array}{ccccccc}
\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{K}\end{matrix}\right\}\mathrm{S}\right) & + & \left(\left.\begin{matrix}\mathrm{Mn}''\\ \mathrm{Cl}^2\end{matrix}\right\}\right) & = & \left(\mathrm{Mn}''\mathrm{S}\right) & + & 2\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{Cl}\end{matrix}\right\}\right)\\
\begin{array}{c}\text{Monosulphide}\\ \text{of potassium.}\end{array} & & \begin{array}{c}\text{Chloride of}\\ \text{manganese.}\end{array} & & \begin{array}{c}\text{Sulphide of}\\ \text{manganese.}\end{array} & & \begin{array}{c}\text{Chloride of}\\ \text{potassium.}\end{array}
\end{array}$$

With acids, hydrosulphates give the same reactions as the monosulphides:

$$\begin{array}{ccccccc}
\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{S}\right) & + & \left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{Cl}\end{matrix}\right\}\right) & = & \left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{Cl}\end{matrix}\right\}\right) & + & \left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{S}\right)\\
\begin{array}{c}\text{Hydrosulphate}\\ \text{of potassium.}\end{array} & & \begin{array}{c}\text{Hydrochloric}\\ \text{acid.}\end{array} & & \begin{array}{c}\text{Chloride of}\\ \text{potassium.}\end{array} & & \begin{array}{c}\text{Hydrosulphuric}\\ \text{acid.}\end{array}
\end{array}$$

But in presence of chloride of manganese, they set free hydrosulphuric acid at the same time as they give rise to a precipitate of sulphide of manganese:

$$\begin{array}{ccccccccc}
2\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{S}\right) & + & \left(\left.\begin{matrix}\mathrm{Mn}''\\ \mathrm{Cl}^2\end{matrix}\right\}\right) & = & \left(\mathrm{Mn}''\mathrm{S}\right) & + & 2\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{Cl}\end{matrix}\right\}\right) & + & \left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{S}\right)\\
\begin{array}{c}\text{Hydrosulphate}\\ \text{of potassium.}\end{array} & & \begin{array}{c}\text{Chloride of}\\ \text{manganese.}\end{array} & & \begin{array}{c}\text{Sulphide of}\\ \text{manganese.}\end{array} & & \begin{array}{c}\text{Chloride of}\\ \text{potassium.}\end{array} & & \begin{array}{c}\text{Hydrosulphuric}\\ \text{acid.}\end{array}
\end{array}$$

The polysulphides precipitate the salts of manganese without disengaging hydrosulphuric acid, but in presence of acids they give both hydrosulphuric acid and a deposit of sulphur:

$$\underset{\substack{\text{Tersulphide of}\\ \text{potassium.}}}{\left(\left.\begin{matrix}K\\K\end{matrix}\right\}S^3\right)} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\substack{\text{Chloride of}\\ \text{potassium.}}}{2\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)} + \underset{\substack{\text{Hydrosulphuric}\\ \text{acid.}}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}S\right)} + \underset{\text{Sulphur.}}{\left.\begin{matrix}S\\S\end{matrix}\right\}}$$

Heat and electricity act on sulphides in the same manner as on oxides.

**Actions of Reagents.**—1st. Action of Sulphur.—Sulphur acts on sulphides as oxygen on oxides; that is to say, it has sometimes no action, and sometimes it causes them to pass to a higher degree of sulphurization.

2nd. Action of Hydrogen.—As hydrogen has a much weaker affinity for sulphur than for oxygen, it necessarily has greater difficulty in reducing sulphides than oxides; nevertheless, there exist sulphides which yield their sulphur to hydrogen, and which are reduced in the same way as the oxides. The sulphide of silver is among the number:

$$\underset{\substack{\text{Sulphide of}\\ \text{silver.}}}{\left(\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}S\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}} = \underset{\substack{\text{Hydrosulphuric}\\ \text{acid.}}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}S\right)} + \underset{\text{Silver.}}{\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}}$$

3rd. Action of Carbon.—Carbon acts on sulphides as on oxides; that is to say, it reduces these bodies, giving rise to a sulphide of carbon:

$$\underset{\substack{\text{Sulphide}\\ \text{of iron.}}}{2(FeS)} + \underset{\text{Carbon.}}{C} = \underset{\substack{\text{Sulphide}\\ \text{of carbon.}}}{(CS^2)} + \underset{\text{Iron.}}{2Fe}$$

This reaction is, however, less frequent than with the oxides.

4th. Action of Chlorine.—By the dry method, chlorine acts on sulphides as on oxides. As with these latter compounds it gives a chloride liberating oxygen, so here it displaces the sulphur, and gives rise to a chloride; the only difference consists in this: oxygen having no affinity for chlorine when hot, remains free when displaced by means of this metalloid; while the sulphur, which can combine with the chlorine, is eliminated in the state of chloride of sulphur.

By the moist method, the chlorine still displaces the sulphur, but then this metalloid remains in a free state instead of combining with the chlorine. This reaction may be readily conceived by remembering that the different chlorides of sulphur are decomposed by water, and consequently cannot arise under conditions where they would be destroyed if formed.

Reaction by the Dry Method.

$$\underset{\substack{\text{Sulphide of}\\ \text{potassium.}}}{\left(\left.\begin{matrix}K\\K\end{matrix}\right\}S\right)} + \underset{\text{Chlorine.}}{2\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}\right)} = \underset{\substack{\text{Chloride of}\\ \text{potassium.}}}{2\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)} + \underset{\substack{\text{Chloride}\\ \text{of sulphur.}}}{(SCl^2)}$$

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### Reaction by the Moist Method.

$$\underset{\text{Sulphide of potassium.}}{2\left(\left.\begin{matrix}\mathrm{K}\\\mathrm{K}\end{matrix}\right\}\mathrm{S}\right)} + \underset{\text{Chlorine.}}{2\left(\left.\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right\}\right)} = \underset{\text{Chloride of potassium.}}{4\left(\left.\begin{matrix}\mathrm{K}\\\mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\text{Sulphur.}}{\left.\begin{matrix}\mathrm{S}\\\mathrm{S}\end{matrix}\right\}}$$

Only one of the different methods of action which chlorine exercises on the oxides is found here; that is, displacement. The union of sulphur with chlorine when hot is a secondary phenomenon, resulting from the reciprocal affinity of these two bodies, which does not diminish the analogy existing between this reaction and that produced with the oxides.

The action of bromine and iodine on the sulphides is identical with that of chlorine.

5th. ACTION OF OXYGEN.—By the dry method, oxygen gives rise to phenomena differing according to the temperature at which the operation is conducted, and according to the sulphide on which it is made to act.

On absorbing oxygen, the sulphide may form a sulphate which cannot be decomposed by heat; or if the sulphide be heated to a temperature insufficient to cause its decomposition, the sulphate is formed:

$$\underset{\text{Sulphide of lead.}}{(\mathrm{PbS})} + \underset{\text{Oxygen.}}{2\left(\left.\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right\}\right)} = \underset{\text{Sulphate of lead.}}{(\mathrm{SPb''O^4})}$$

If the temperature be sufficiently elevated, and the sulphate of the metal whose sulphide we possess, be too slightly stable to be formed under the conditions of the experiment, an oxide is produced, and sulphurous anhydride is disengaged:

$$\underset{\text{Sulphide of copper.}}{2(\mathrm{Cu''S})} + \underset{\text{Oxygen.}}{3\left(\left.\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right\}\right)} = \underset{\text{Oxide of copper.}}{2(\mathrm{Cu''O})} + \underset{\text{Sulphurous anhydride.}}{2(\mathrm{SO^2})}$$

If the oxide itself is not stable at the temperature at which the operation is conducted, the sulphur is eliminated in the state of sulphurous anhydride, and the body with which it was first combined becomes free:

$$\underset{\text{Sulphide of platinum.}}{(\mathrm{Pt^{iv}S^2})} + \underset{\text{Oxygen.}}{2\left(\left.\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right\}\right)} = \underset{\text{Sulphurous anhydride.}}{2(\mathrm{SO^2})} + \underset{\text{Platinum.}}{\mathrm{Pt}}$$

By the moist method, oxygen has a double action; it displaces a portion of the sulphur and gives rise to an oxide. The sulphur displaced unites with the sulphide undecomposed, and forms a polysulphide, but this action is shortly arrested, and the oxygen acting on the sulphide, transforms it into a mixture of hyposulphite and hydrate :

$$\underset{\text{Sulphide of potassium.}}{4\Big(\left.\begin{matrix}K\\K\end{matrix}\right\}S\Big)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} = \underset{\text{Oxide of potassium.}}{2\Big(\left.\begin{matrix}K\\K\end{matrix}\right\}O\Big)} + \underset{\text{Bisulphide of potassium.}}{2\Big(\left.\begin{matrix}K\\K\end{matrix}\right\}S^2\Big)}$$

$$\underset{\text{Sulphide of barium.}}{4\big(Ba''S\big)} + \underset{\text{Oxygen.}}{4\Big(\left.\begin{matrix}O\\O\end{matrix}\right\}\Big)} + \underset{\text{Water.}}{2\Big(\left.\begin{matrix}H\\H\end{matrix}\right\}O\Big)} = \underset{\text{Hyposulphite of barium.}}{2\big(S^2BaO^3\big)} + \underset{\text{Hydrate of barium.}}{2\Big(\left.\begin{matrix}Ba''\\H^2\end{matrix}\right\}O^2\Big)}$$

All these reactions present the most perfect parallelism with those resulting from the action of sulphur on the oxides.

6th. Action of Metals.—When a metal is made to act on a metallic sulphide, and when this metal has a greater affinity for sulphur than that which is combined with this body, it seizes the sulphur and the other metal is liberated.

$$\underset{\text{Sulphide of lead.}}{(Pb''S)} + \underset{\text{Iron.}}{Fe} = \underset{\text{Sulphide of iron.}}{(FeS)} + \underset{\text{Lead.}}{Pb}$$

7th. Action of Water.—Certain sulphides, like the sulphide of magnesium, decompose water, producing an oxide and sulphuretted hydrogen :

$$\underset{\text{Sulphide of magnesium.}}{\big(MgS\big)} + \underset{\text{Water.}}{\Big(\left.\begin{matrix}H\\H\end{matrix}\right\}O\Big)} = \underset{\text{Oxide of magnesium.}}{\big(MgO\big)} + \underset{\text{Hydrosulphuric acid.}}{\Big(\left.\begin{matrix}H\\H\end{matrix}\right\}S\Big)}$$

Other sulphides can combine with water ; but when hot the water is decomposed, and, as in the preceding case, an oxide is formed and sulphuretted hydrogen, but most of the sulphides have no action on water.

8th. Action of Hydrosulphuric Acid.—Hydrosulphuric acid enters into double decomposition with the alkaline sulphides, and gives rise to a hydrosulphate which is a sulpho-base ; this reaction is analogous to that produced when water and an anhydrous alkaline oxide are brought into contact :

$$\underset{\text{Sulphide of potassium.}}{\Big(\left.\begin{matrix}K\\K\end{matrix}\right\}S\Big)} + \underset{\text{Hydrosulphuric acid.}}{\Big(\left.\begin{matrix}H\\H\end{matrix}\right\}S\Big)} = \underset{\text{Hydrosulphate of potassium.}}{2\Big(\left.\begin{matrix}K\\H\end{matrix}\right\}S\Big)}$$

The action of hydrosulphuric acid on the basic anhydrosulphides has not as yet been examined.

9th. Action of Acid Anhydrosulphides.—These combine with basic anhydrosulphides, or undergo double decomposition with them, and sulpho-salts are formed.

10th. Action of Basic Anhydrosulphides.—These combine with acid anhydrosulphides, or enter into double decomposition with them, and give rise to sulpho-salts.

It will be seen that the actions of reagents on sulphides present the strictest analogies with the actions of reagents on oxides. In order to demonstrate these analogies more fully, we place these different reactions side by side.

## PARALLEL BETWEEN SULPHIDES AND OXIDES.

| Sulphides. | Oxides. |
|---|---|
| Action of Heat.—It reduces them, or does not attack them. | Action of Heat.—It reduces them, or does not attack them. |
| Action of Sulphur.—It transforms them into persulphide, or has no action. | Action of Oxygen.—It peroxidizes them, or has no action. |
| Action of Hydrogen.—It reduces them :<br>$(M^2S) + H^2 = (H^2S) + M^2$.<br>or does not modify them at all. | Action of Hydrogen.—It reduces them :<br>$(M^2O) + H^2 = (H^2O) + M^2$<br>or does not modify them at all. |
| Action of Carbon.—This action is either reducing or none. The reducing action is expressed by the general formula :<br>$C + 2(M^2S) = 2M^2 + (CS)^2$ | Action of Carbon.—This action is either reducing or none. The reducing action is expressed by the general formula :<br>$C + 2(M^2O) = 2M^2 + (CO)^2$. |
| Action of Chlorine.—It seizes the electro-positive element and liberates the sulphur, only the excess of the chlorine unites with the sulphur displaced. | Action of Chlorine.—It seizes the electro-positive element and liberates the oxygen. |
| Action of Oxygen.—By the dry method, and according to the degree of stability of the compounds which arise, there is formed either sulphurous anhydride and an oxide, or sulphurous anhydride and a metal, or a sulphate ; by the moist method, a mixture of hydrated oxide and hyposulphite is produced. | Action of Sulphur.—By the dry method, and according to the degree of stability of the compounds which arise, there is formed either sulphurous anhydride and a sulphide, or sulphurous anhydride and a metal, or a sulphate ; by the moist method, a sulphide and a hyposulphite are produced. |
| Action of Metals.—The most positive metals displace those that are less so. | Action of Metals.—The most positive metals displace those that are less so. |
| Action of Hydrosulphuric Acid.—This acid sometimes produces | Action of Water.—Sometimes it produces acid hydrates, some- |

acid hydrosulphates, sometimes basic hydrosulphates, sometimes indifferent hydrosulphates, and sometimes it has no action.

Action of Basic Anhydrosulphides.—They react on the acid anhydrosulphides and give sulphosalts.

Action of Acid Anhydrosulphides.—They react on basic anhydrosulphides to form sulphosalts.

Action of Acids.—They react on the basic metallic sulphides, giving a salt and sulphuretted hydrogen:

$$\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right) + \left(\left.\begin{matrix}K\\K\end{matrix}\right\}S\right) = \left(\left.\begin{matrix}SO^{2''}\\K^2\end{matrix}\right\}O^2\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}S\right)$$

times basic hydrates, sometimes indifferent hydrates, and sometimes it has no action.

Action of Basic Anhydrides.—They react on acid anhydrides and give salts.

Action of Acid Anhydrides.—They react on basic anhydrides to form salts.

Action of Acids.—They react on basic anhydrides, giving rise to water and to a salt.

$$\left(\left.\begin{matrix}So^{2''}\\K^2\end{matrix}\right\}O^2\right) + \left(\left.\begin{matrix}K\\K\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}SO^{2''}\\K^2\end{matrix}\right\}O^2\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

## GENERAL REMARKS ON CHLORIDES.

**Preparation.**—Chlorides may be obtained:

1st. By burning in chlorine the elements to be combined with this metalloid. The chlorides of phosphorus, arsenic, antimony, sulphur, tin, copper, iron, etc., may be prepared in this way.

2nd. By transmitting a current of chlorine over the anhydrous oxides; the oxygen is then displaced. This method is employed in the preparation of the chlorides of nickel and cobalt:

$$\underset{\text{Oxide of cobalt.}}{2\left(CoO\right)} + \underset{\text{Chlorine.}}{2\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}\right)} = \underset{\text{Chloride of cobalt.}}{2\left(\left.\begin{matrix}Co''\\Cl^2\end{matrix}\right\}\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}}$$

3rd. By causing hydrochloric acid to act on the metals:

$$\underset{\text{Monatomic metal.}}{\left.\begin{matrix}M\\M\end{matrix}\right\}} + \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\text{Metallic chloride.}}{2\left(\left.\begin{matrix}M\\Cl\end{matrix}\right\}\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}}$$

4th. By submitting the elements to be chlorinated to the action of aqua regia.

5th. By causing hydrochloric acid to act on the oxides. Water is formed in the reaction:

$$\underset{\text{Metallic oxide.}}{\left(M^2O\right)} + \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\text{Metallic chloride.}}{2\left(\left.\begin{matrix}M\\Cl\end{matrix}\right\}\right)} + \underset{\text{Water.}}{\left(H^2O\right)}$$

6th. By heating a simple body with the chloride of another simple body which has less affinity for chlorine than the first has. For instance, the chloride of antimony is obtained by heating antimony with the bichloride of mercury:

$$\underset{\text{Bichloride of mercury.}}{3\left(HgCl^2\right)} + \underset{\text{Antimony.}}{\begin{matrix}Sb\\Sb\end{matrix}} = \underset{\text{Chloride of antimony.}}{2\left(\left.\begin{matrix}Sb\\Cl^3\end{matrix}\right\}\right)} + \underset{\text{Mercury.}}{3Hg.}$$

**Classification.**—Starting from the fact that certain chlorides combine among themselves forming double chlorides, some chemists, who do not admit the atomic theory, have compared this reaction to the combination of oxygenated basic anhydrides with the acid anhydrides. They have consequently applied the same classification to chlorides as to oxides, and admitted the existence of acid, basic, indifferent, and saline chlorides.

Modern ideas are opposed to this view: monatomic chlorine cannot give reactions analogous to those given by biatomic oxygen. Double chlorides are not true atomic combinations. They can only be explained by being considered as molecular combinations analogous to those compounds which contain water of crystallization. Considered as atomic compounds, their existence would no longer come within the general laws of the atomicity of the elements, or at least would oblige us to consider the atomicity of chlorine as three, which is possible, but which has not yet been proved.

The classification of the chlorides found in almost all elementary works can therefore no longer be used; we will substitute that proposed by Gerhardt, which consists in arranging chlorides in two classes, that of the *negative chlorides* and that of the *positive chlorides.*

The negative chlorides are those which give rise to acids on losing their chlorine and taking the residue OH in exchange for this metalloid.

The positive chlorides are those which by an analogous substitution, produce bases.

Thus, the chloride of silicon ($SiCl^4$) may lose its four atoms of chlorine and take four molecules of the OH group in exchange; it is then transformed into silicic acid $\left(Si^{iv}\left\{\begin{matrix}OH\\OH\\OH\\OH\end{matrix}\right.\right) = \left(\left.\begin{matrix}Si^{iv}\\H^4\end{matrix}\right\}O^4\right)$. It is a negative chloride.

The perchloride of iron, on the contrary, gives a base, when its six atoms of chlorine are replaced by six times the residue OH. It is a positive chloride.

**Distinctive Characteristics of Chlorides.**—All chlorides are soluble in water with the exception of the chloride of silver and mercuric chloride, which do not dissolve in it at all; the chloride of lead, which it scarcely dissolves when cold; and the cuprous chloride, of which it dissolves a very small proportion.

Hydrochloric acid and the soluble chlorides give white precipitates with nitrate of silver. The precipitate is curdled but easily agglomerated, and becomes black in the light. It is soluble in ammonia, in cyanide of potassium and in hyposulphite of sodium; acids do not dissolve it.

The protonitrate of mercury in the solutions of chlorides produces a white precipitate of protochloride of mercury; ammonia does not dissolve this precipitate, but transforms it into protoxide of mercury of a black colour.

Chlorides when heated with sulphuric acid and bichromate of potassium give a red liquid, which is the chloride of chromyl ($CrO^2Cl^2$), and which, when saturated by ammonia, is yellow, in consequence of the formation of chromate of ammonium.

## GENERAL REMARKS ON BROMIDES, IODIDES, AND FLUORIDES.

All the explanations we gave, when speaking of the preparation of chlorides, of their properties and their classification, also apply to these three saline groups, and it only remains for us to indicate the distinctive characteristics of each of them.

**Bromides.**—With the exception of the bromide of silver and protobromide of mercury, which are insoluble; the bromide of lead and the sub-bromide of copper, which are very slightly soluble, all the bromides are soluble in water.

Hydrobromic acid and the soluble bromides give, with nitrate of silver, a yellowish-white curdled precipitate of bromide of silver, which quickly blackens by exposure to the light. This precipitate dissolves in ammonia, in cyanide of potassium, and in hyposulphite of sodium; its solubility in ammonia is less than that of the chloride.

If chlorinated water be added to the solution of a bromide, the bromine is liberated; on shaking the liquid with ether, this dissolves the bromine, and when left at rest it forms a brown layer, which floats on the surface of the liquid.

On heating a bromide with a mixture of sulphuric acid and peroxide of manganese, a disengagement of bromine, which is readily recognized by its odour and colour, takes place.

**Iodides.**—The number of insoluble iodides is much larger than that of the chlorides and bromides possessing the same property.

Soluble iodides and hydriodic acid give, with nitrate of silver, a yellowish-white precipitate of iodide of silver. This precipitate is very sparingly soluble in ammonia, but it readily dissolves in the solution of cyanide of potassium or hyposulphite of sodium.

In presence of sulphate of copper, iodides give a precipitate of subiodide of copper, which is soluble in ammonia, in hyposulphite of sodium, and in cyanide of potassium; at the same time a certain quantity of iodine is liberated according to the equation:

$$\underset{\text{Sulphate of copper.}}{2\left(\left.\begin{matrix}SO^{2''}\\Cu''\end{matrix}\right\}O^2\right)} + \underset{\text{Iodide of potassium.}}{4\left(\left.\begin{matrix}K\\I\end{matrix}\right\}\right)}$$

$$= \underset{\text{Sulphate of potassium.}}{2\left(\left.\begin{matrix}SO^{2''}\\K^2\end{matrix}\right\}O^2\right)} + \underset{\text{Subiodide of copper.}}{\left(\left.\begin{matrix}Cu^{2''}\\I^2\end{matrix}\right\}\right)} + \underset{\text{Iodine.}}{\left.\begin{matrix}I\\I\end{matrix}\right\}}$$

The nitrate of palladium causes the formation of a black precipitate in the solutions of iodides.

When starch is added to the solution of an iodide, and a few drops of chlorinated water added to liberate the iodine, the starch assumes a characteristic beautiful blue colour. If too much chlorine be added, the iodine will pass to the state of iodic acid, and the blue colour will disappear. It will again reappear if a little hydrogen be disengaged in the liquid by means of zinc and sulphuric acid.

If a solution of an iodide be shaken with sulphide of carbon, after liberating the iodine by means of a solution of chlorine the sulphide of carbon assumes a violet colour.

The iodides produce a red precipitate in solutions of the per-salts of mercury. This precipitate is soluble in an excess of either of the two precipitants.

Heated with sulphuric acid, iodides disengage beautiful violet vapours of iodine.

**Fluorides.**—Soluble fluorides and hydrofluoric acid produce in the solutions of barytic salts a white precipitate of fluoride of barium, which dissolves when a few drops of hydrochloric or nitric acid are added to the liquid.

Nitrate of calcium gives a precipitate which is insoluble in acetic acid, but soluble in nitric acid.

When a fluoride is heated with concentrated sulphuric acid and silica, gaseous fluoride of silicon is disengaged, which, on contact with water, gives a precipitate of gelatinous silica.

A fluoride submitted to the action of boiling sulphuric acid disengages hydrofluoric acid, which destroys glass.

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# APPENDIX.

## PROUT'S HYPOTHESIS.

For a long time philosophers have been disposed to admit that all matter is one and the same, and that the numerous substances we see are only different manifestations of it—manifestations, the diversity of which depend upon the degree of its condensation. This idea, well explaining the fact that gravity acts equally on all bodies, and answering moreover to the idea we have, rightly or wrongly, of the simplicity of the great laws of nature, is introduced into science. A very short time ago, an English chemist, Mr. Graham, admitted, in speculations on the constitution of matter, that chemical atoms are formed by an agglomeration of particles smaller than themselves and identical, to which he gave the name of ultimates; these ultimates are animated by vibratory movements, the variable length of which in different bodies causes the differences observed between these.

At the commencement of this century, an English chemist, Prout, wished to give to this theory of the unity of substance an experimental proof. He asserted that *the atomic weights of all simple bodies are exact multiples of the atomic weight of hydrogen.* Thence it was only one step to consider all bodies as polymers of hydrogen.

Prout's hypothesis was among the number of those of which it is not easy to demonstrate either the accuracy or inaccuracy, especially at the time it was published : the atomic weight of hydrogen, being very small in relation to that of the heavy metals, it was scarcely possible to know whether the differences observed were real or the result of errors of observation. But as analytic methods improved, the causes of uncertainty diminished, and it soon became evident that, as it was then expressed, Prout's hypothesis was inadmissible.

In order to suit the hypothesis to facts, M. Dumas modified its enunciation ; and in a pamphlet published by him in 1859, he admitted that *the atomic weights of all bodies are the exact multiples of that of an unknown body which would have an atomic weight four times smaller than hydrogen* ; or, what comes to the same thing, *that the atomic weights of all bodies are the exact multiples of that of hydrogen by* 1, *by* 0·50 *or by* 0·25.

As Prout's hypothesis was independent of the unit adopted, and could be admitted for a body which had no real existence, quite as well as for hydrogen, this new enunciation satisfied the partizans of unity of substance.

After M. Dumas' pamphlet, the question appeared to be decided in favour of Prout's hypothesis, but in 1860 M. Stas published his researches on nitrogen, chlorine, sulphur, potassium, lead, and silver, which were made with extraordinary precision, and the conclusion of which was: "*There exists no common divisor among the weights of simple bodies which unite to form definite combinations, and Prout's law is a pure illusion.*"

M. Marignac, without contesting the value of these researches, on the exactness of which he greatly rested, raised an objection. "If," said he, "in stable chemical combinations the constituting elements were not invariably and exactly in the proportion of their atomic weights, all the most exact methods of analysis and synthesis would give the proportions of these weights with the same inexactness."

This was bringing the whole of chemistry into question, for the idea of atoms or equivalents is founded on the law of definite proportions, regarded not as a limited, but as a mathematical law.

The argument of M. Marignac was, nevertheless, not without foundation. The constancy of composition of combinations called stable might, it is true, be considered to be proved after all the analyses of the century; but does the proportion in weight which the elements assume in a combination remain the same when these elements enter into new combinations? This was what had been admitted rather by intuition than from absolute proof. Wenzel, it is true, had founded this law on the constancy of the neutrality of the saline solutions which reciprocally precipitate each other; but the preservation of neutrality, proved by test papers, was certainly not a sufficient proof.

M. Stas, in an important memoir read 14th July, 1865, at the Academy of Sciences at Brussels, records a series of experiments appropriate for the decision both of the problem given by Prout and that given by Marignac. He first showed that by precipitating nitrate of silver by chloride of ammonium, and using chloride of ammonium prepared at different temperatures and under different pressures, that the proportional relation of silver and chloride of ammonium remains constant. Temperature therefore exercises no action on the composition of chloride of silver, and neither temperature nor pressure influence the composition of chloride of ammonium. *The constancy of the composition of stable bodies* is thus demonstrated.

M. Stas has also shown *the invariability of the proportions in weight of the elements forming chemical combinations.* He found that the iodate, bromate, and chlorate of silver are transformed into iodide, chloride, and bromide of silver under the influence of sulphurous anhydride, without the smallest particle of iodine or silver being liberated. This could not be, except on the condition that the proportion of silver to the halogen metalloid be the same in the binary and ternary compounds of this metal, and this was what was in question. If, in effect, in two bodies AB and ABC the proportion $\frac{A}{B}$ were not the same, ABC could only be transformed into AB by losing part of either A or B.

After having firmly demonstrated this fundamental law on which the whole of chemistry rests, M. Stas has very carefully shown the atomic weights of a certain number of bodies. For this purpose he used new and very precise methods. He always deduced the atomic weight of a given element from the compounds formed by this element with several different bodies. He has thus checked his numbers, and at the same time has given another indirect but weighty proof of the invariability of the proportion in weights of the elements forming chemical compounds.

The limits of this work do not permit us to enter further into detail on these experiments. We will simply give their results.

| | |
|---|---|
| If oxygen be arbitrarily made equal to . . | 16 |
| The atomic weight of silver is . . . . . . | 107·93 |
| Nitrogen . . . . . . . . . . . . . | 14·044 |
| Bromine . . . . . . . . . . . . . | 79·952 |
| Chlorine . . . . . . . . . . . . . | 35·457 |
| Iodine . . . . . . . . . . . . . | 126·850 |
| Lithium . . . . . . . . . . . . . | 7·022 |
| Potassium . . . . . . . . . . . . . | 39·137 |
| Sodium . . . . . . . . . . . . . | 23·043 |

Which numbers are in accordance with those deduced from the experiments made in 1843 by M. Marignac.

These numbers are in relation to oxygen, made, as we have said, arbitrarily equal to 16; but, according to M. Stas, oxygen is not 16: if hydrogen = 1, it is 15·96. They ought all therefore to undergo a proportional reduction, and will then become:

H = 1
O = 15·960
Ag = 107·660
N = 14·009
Br = 79·750

Cl = 35·368
I = 126·533
Li = 7·004
K = 39·040
Na = 22·980

These figures entirely nullify Prout's hypothesis.

# PART THIRD.

## ORGANIC CHEMISTRY.

## GENERAL OBSERVATIONS.

In the early stages of chemistry it was understood how to decompose and reconstruct most of the inorganic compounds known up to that time; but it was not so when it became a question of principles extracted from living bodies: of these the definite combinations (proximate principles) were known, but they could not be produced synthetically by the combination of their elements. It was believed that life was necessary to their formation, and they were considered absolutely distinct from inorganic compounds. Hence arises the division of chemistry into organic and inorganic.

However, as the science progressed it was perceived that the most complete identity existed between the reactions of organic and those of inorganic chemistry, and that by introducing new elements into organic compounds, and acting on the latter by oxidation, reduction, substitution, etc., it was possible to obtain substances of which no trace was found in living bodies. Later still, one of the principles of the urine —urea—was obtained by the help of cyanates and ammoniacal salts, which can both be prepared from their elements. Then the barrier which separated the two divisions of chemistry was overcome, and it became possible to hope that some day all the organic products might be prepared synthetically. This hope has, to a great extent, been realized by the remarkable labours of MM. Kolbe, Berthelot, Wurtz, Kékulé, Cannizzaro, Perkins, Duppa, Maxwell Simpson, Harnitzky, Lippmann, and others. At the present day, therefore, there are no longer two distinct chemistries; there is only one, within which is contained the study of the compounds called organic.

In reality, organic chemistry is simply that part of the science which relates to the series of carbon compounds. It would have been more regular to study this series after carbon, as we have studied the combinations formed by the other elements after each of them.

Nevertheless, we have abandoned the logical course to re-enter the paths of the past; the reason for this is simple:

Carbon enters into so great a number of compounds that the study of these demands at least as much space as that for the compounds formed by all the other elements united. And further, the combinations into which carbon enters are often highly complicated. We there meet radicles which act sometimes as metals, sometimes as metalloids. In short, it is almost impossible to understand the series of carbon compounds, if all the other simple bodies, and the compounds which they form, have not been previously studied.

To include organic with inorganic chemistry would therefore be proper in a book intended exclusively for the learned, but would not be convenient in a work designed for general use. We have therefore preserved the division of chemistry into organic and inorganic, and shall content ourselves with pointing out that this division is altogether artificial, and only made to meet the requirements of the student.

We must establish a very important distinction before commencing. *Organic* must not be confounded with *organized* bodies. Organic substances, whatever their origin, are, as we have just said, bodies which possess all the properties of definite compounds. When solid, they crystallize; when liquid, they have a fixed boiling point; they do not differ in any way from inorganic compounds.

Organized bodies, on the contrary, are always constituted by the mixture of a great number of compounds. They never present a crystalline structure, but a well-marked fibrous or cellular one, and they cannot change their condition without being destroyed. Finally, all are, or have been, endowed with life. They are organs, or parts of organs, of which the chemist can never accomplish the synthesis, however perfect his means of action.

The study of organized bodies does not belong to the domain of chemistry, but rather to that of biology. If at this point biology approaches to chemistry, it is entirely to borrow light from it, as chemistry itself borrows from physics, and physics from mathematics, without each ceasing to be a distinct science. It is solely because this distinction has not been universally perceived, that in almost all treatises on chemistry, articles are found devoted to the blood, muscles, etc., which ought only to be contained in works on physiology.

## ORGANIC ANALYSIS.

The organic analyst may have two problems to solve. Either a mixture of different organic bodies being given, he seeks to separate them from each other without altering their composition, which is termed proximate analysis; or a definite compound having been obtained in a pure state, he seeks to determine the nature and quantity of the elements which enter into its composition. This is termed ultimate analysis.

**Proximate Analysis.**—We may have a mixture containing fixed solid substances, liquid substances either volatile or not, volatile solid substances, and gases.

If the solids and gases do not dissolve in the liquids, these bodies must first be mechanically separated and then the appropriate methods of analysis must be applied to each.

If, on the contrary, the solid substances and the gases are dissolved in the liquids, the mass should first be distilled. Under the influence of heat, the gases will be first eliminated and are collected over mercury, then the liquid will pass over by distillation, and, finally, the fixed matter will remain in the retort.

If the mixture contain a volatile solid body, this will pass over by distillation at the same time as the liquids, and must then be separated from these latter by processes which enable the different definite principles it contains to be extracted from a given liquid.

Finally, if we have a mixture of solid and liquid substances which are neither of them volatile, a common method of analysis must be applied to both. In this latter case, the separation of the different definite compounds which the mixture contains is always very difficult, and sometimes impossible.

Separation of the Definite Compounds contained in a Mixture of Solid Bodies.—Neutral solvents such as water, alcohol, ether, wood spirit, sulphide of carbon, benzine, or chloroform, are made to act successively on the substances. These liquids each dissolve certain matters and leave others as a residue; they have, moreover, the advantage of not altering them.

When the substance has been thus divided into a certain number of distinct parts, each of these is again submitted to the action of different neutral solvents. Thus the residue of the aqueous solution will be submitted to the action of alcohol, ether, etc. These different operations are only stopped when the different products obtained are all found to have a definite composition. (We shall see further on by what characters the purity of a compound may be recognized.)

Often, though soluble in different degrees in the various neutral liquids, the substances which constitute a mixture are all soluble or all insoluble in each of these taken separately. Fractional solution or fractional crystallization must then be employed.

Fractional solution consists in the successive action of quantities of the same liquid, each of which must be insufficient to dissolve the whole of the mass submitted to its action. The most soluble substances are then found in the first solutions, and the least soluble in the last. On evaporating the solutions, and again submitting the residues to similar treatment, the different principles the mixture contained will at last be separated. For example, let us suppose a mixture of two bodies A and B in equal proportions, and that 100 gr. of water can dissolve 50 gr. of A and 25 gr. of B. Let us now see what would happen if successive weights of water equal to 50 gr. were made to act on 200 gr. of the substance.

Each 50 gr. of water would dissolve 25 gr. of A and 12·50 of B. So that after renewing the liquid four times, the whole of the body A would be eliminated, while there would remain 50 gr. of B in a state of purity.

The solution of a mixture of solid bodies may also be evaporated, and the crystals separated as they form. The least soluble substances crystallize first, and the most soluble afterwards. By repeating these crystallizations several times, the desired separation is effected; the different crystalline deposits should be carefully examined. When the crystals obtained appear to be homogeneous, there is reason to believe that the substance is pure.

When all the neutral solvents leave an insoluble residue, this is submitted to the action, first, of dilute mineral acids, afterwards of bases. The organic acids and bases are thus transformed into salts soluble in water; on applying to these salts the method of fractional solutions or crystallizations, and separating the acids or bases from them, the bodies are obtained in a pure state.

When the acids or bases whose elements are found in solution can be precipitated by appropriate reagents, the proximate analysis is made by causing the precipitation by successive quantities of the reagents each insufficient to precipitate the whole; the least stable salts precipitate first, and the most stable afterwards. By applying this method to the salts of margaric acid, and repeating these fractional precipitations about forty times, M. Heintz has been enabled to show that this body is not a definite principle, but a mixture of two other acids.

SEPARATION OF DEFINITE COMPOUNDS CONTAINED IN A MIXTURE OF LIQUID BODIES.—As these liquids do not always mix with each other in all proportions, the method of fractional solutions may often be applied to them; it is even the only one to which recourse can be had if the liquid is not volatile. But, as here we cannot be aided by the crystalline form in judging of the purity of the substances, this process presents great difficulties.

When liquids distil without decomposing, the method of fractional distillations may be employed. This method is based on the fact that all pure liquids have a constant boiling point, while mixtures of different liquids commence boiling at a temperature which rises as the distillation proceeds. On collecting separately the products which have distilled between the limits of the temperature, and submitting these latter again to fractional distillation, we are often able to separate from each other liquids, the boiling points of which are different. This method, to be successfully employed, requires that the liquids mixed have boiling points differing at least thirty degrees, and that the chemist should have at his disposal a rather large quantity of the mixture.

It sometimes happens that two mixed liquids, though not reacting chemically, nevertheless exercise on each other a physical action which is opposed to their separation by fractional distillation. The mixture then presents a constant boiling point.

Organic compounds generally begin to decompose at about 400° : it is scarcely possible to apply fractional distillation to liquids whose boiling point is higher than this. The field of this operation may, however, be extended by distilling under a low pressure, because the boiling point of liquids is thereby considerably lowered.

Fractional distillation in vacuo takes place in the apparatus represented in fig. 37.

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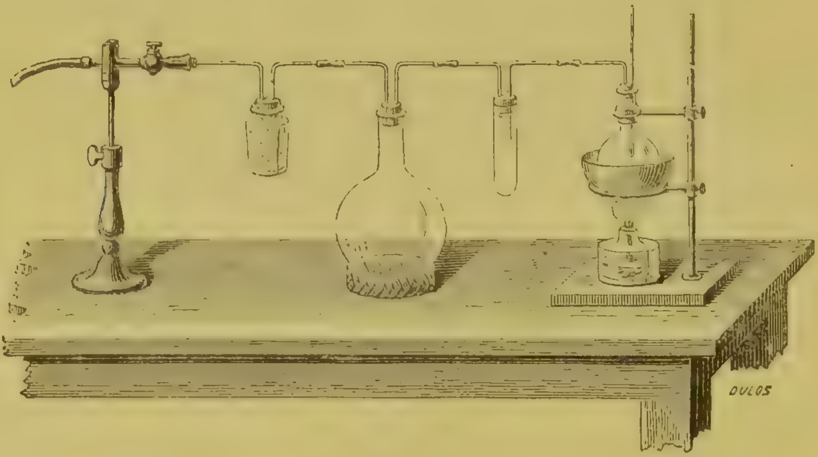

Fig. 37.

The liquid to be distilled is placed in a strong globe, the neck of which is tightly closed by an india-rubber stopper with two holes in it. One of these holes contains a thermometer, and the other has a tube of exit in it. This tube is joined by means of very tight india-rubber to a similar one which conducts the vapours into a tube of thick glass, which acts as a receiver, and which is also closed by an india-rubber stopper with two openings. A disengagement tube fixed in one of these openings is placed in communication with a large globe by means of india-rubber and another glass tube. After this globe comes a vessel filled with pumice-stone saturated with a solution of caustic potash. The tube which conducts the gases is plunged to the bottom of this vessel, in order that the acid vapours or the chlorinated products which sometimes disengage during the distillation be absorbed, and do not affect the apparatus.

The tube which gives egress to the gases of this latter vessel is joined by means of a good stopper to a brass tubulure, to which a long india-rubber tube is fastened. This tube is strengthened by a spiral copper wire in its interior, in order that its sides may not be compressed under the influence of atmospheric pressure while a vacuum is being made. The india-rubber tube is terminated by a brass stop-cock, to which it is fastened, and which is screwed on to the air-pump.

The globe containing the substance is generally heated in a bath of oil by means of a spirit-lamp. The second globe is not strictly necessary, but it is useful: by augmenting the space in which the vacuum is made, it serves to render less perceptible the differences of pressure resulting from the entrance of the air, which can never be entirely prevented. While the operation continues, it is necessary to pump from time to time, in order to maintain a regular pressure.

To the method of fractional distillations, we should also add that of fractional saturations, which are of great service when the liquid is acid or basic.

If to a mixture of two volatile acids a quantity of base be added which is insufficient to saturate all, the strongest acid is first saturated. If more base be employed than is required to saturate this completely, a portion of the second acid is also saturated; and when the mixture is distilled, the non-saturated portion of the second acid distils alone, and is thus isolated in a pure state.

If, on the contrary, less of the base be employed than is necessary to saturate the stronger acid, part only of this latter is saturated, but not even the smallest quantity of the other enters into the combination. On distilling, a mixture of the two acids is collected, and a perfectly pure salt of the stronger acid remains in the retort.

It will be seen that a single operation gives one of the products in a pure state, and that with two successive operations both can be isolated. We have only to submit the mixture which remains after the first fractional saturation to a new fractional saturation. This process of proximate analysis may also be applied to volatile alkaloids; of course using an acid instead of a base.

SEPARATION OF GASES.—We cannot enter in detail into the processes used for the proximate analysis of gases; physical means can here scarcely be made use of, and it is chiefly by absorbing the different gases by appropriate reagents that they can be separated.

Cuprous chloride dissolved in ammonia, the Nordhausen sulphuric acid, potash, bromine, protosulphate of iron, permanganate of potash, and phosphorus are the reagents most frequently used. Oxygen is absorbed by the ammoniacal cuprous chloride, which does not again set it free; by the oxide of carbon, which parts with it on boiling, and by certain carbides of hydrogen, such as acetylene or allylene. With these latter it forms insoluble solid compounds, which may be separated by filtration, and from which the primitive gas may be afterwards disengaged in a free state under the influence of hydrochloric acid.

Nordhausen sulphuric acid and bromine absorb certain hydro-carbons. With bromine, these form liquid products which can be separated by fractional distillations.

Potash absorbs carbonic anhydride; protosulphate of iron and permanganate of potash absorb the binoxide of nitrogen, and phosphorus absorbs oxygen.

CHARACTERS WHICH SERVE TO DETERMINE WHETHER AN ORGANIC MATTER MAY BE REGARDED AS CONSISTING OF A SINGLE PRINCIPLE.—When the substance is solid, this may be recognized by the following characters:

1st. If it be capable of melting, the temperature remains constant during the whole time occupied by the fusion.

2nd. If it crystallize, its crystals are all perfectly homogeneous.

3rd. When submitted to the action of different solvents, it either will not dissolve at all or it dissolves totally, provided that a sufficient quantity of the liquid be employed.

4th. When it is divided into several parts by means of fractional solutions, the weights of the different residues arising from the evaporation of equal quantities of the solvent are equal; moreover, these different residues present the same physical characters, and ultimate analysis assigns to them the same composition.

When the substance is liquid, it presents a constant boiling point; but, as we said before, the constancy of the boiling point is not alone sufficient for us to affirm that a substance is constituted of a single principle, inasmuch as certain mixtures possess this property, this constancy must exist under all pressures. It is observed that the relation between the tensions of the vapours of two liquids changes with the temperature. As by lowering the pressure the boiling point is also lowered, the relation between the elastic forces of the vapours of the mixed liquids changes, and with it the quantities of each of them which distil. The result is that, by distillation in vacuo, liquids may be separated, which at a normal pressure form a mixture, the boiling point of which is constant.

**Ultimate Analysis.**—The object of ultimate analysis is to determine the proportions of the different simple elements which enter into the composition of an organic body. As all organic compounds contain carbon, and nearly all contain hydrogen, the determination of these two bodies, or at least of one of them, is always necessary. Besides, as it is often necessary to determine the chlorine, bromine, iodine, nitrogen, phosphorus, arsenic, sulphur, and metals, we will successively review these different analyses.

1st. DETERMINATIONS OF CARBON AND HYDROGEN.—This is based on the property possessed by chromate of lead and by oxide of copper, of oxidizing organic substances while they themselves are deoxidized. In this combustion the hydrogen of the organic substance passes into the state of water, and the carbon into that of carbonic anhydride. These bodies are collected in apparatus previously weighed, their weights ascertained, and that of the carbon and hydrogen thence deduced.

This analysis requires minute precautions. The oxide of copper must first be heated to redness in order to destroy the organic particles which might be deposited upon it, and to drive off the hygrometric moisture; then, while it is still warm, it is enclosed in a clean and very dry bottle, which is closely stoppered, and in which it can become cool without absorbing moisture. Generally, the bottle is rinsed out two or three times with hot oxide of copper, which is rejected, and it is only after these preliminary operations that the bottle is filled. This washing with oxide of copper is for the purpose of completely drying the bottle and removing all solid substances from it.

A hard glass tube, about thirty inches in length and half an inch in diameter, is used. The form represented in fig. 38 is given to this tube by drawing it out at one of its ends. The inside should be dried by bibulous paper, then cleansed with heated oxide of copper, and, finally, carefully stoppered until the time of the analysis.

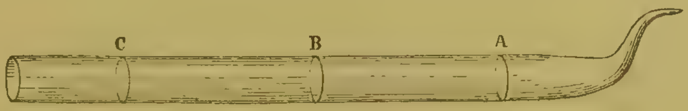

Fig. 38.

Then the substance to be analysed is prepared. If this be solid, it is powdered and dried in a small stove heated to 100°, until no loss is observed after two successive weighings. A very dry small glass tube is then filled with it, and carefully stoppered and weighed.

This done, a certain quantity of oxide of copper is put into the tube, as far as A for instance; then the small tube is uncorked, and the substance to be analyzed is allowed to fall into the larger tube. More oxide of copper is added, and by means of a long copper rod, the lower part of which is twisted in a spiral form, the substance is mixed with this oxide, so that the mixture occupies about the space comprised in the drawing between A and B; finally, from B to C the tube is filled with pure oxide of copper, after which it is well corked. The small tube which first contained the substance is then weighed, and on deducting this weight from its weight when full, that of the substance to be analyzed is obtained.

The combustion tube is next wrapped in a sheet of iron, in order that it may not be distorted by the heat, and the mouth is closed by a good cork, through which it is placed in communication with the condensing apparatus destined to absorb the water and the carbonic anhydride.

The apparatus used to absorb the water is composed of a U-shaped tube full, either of pumice-stone moistened with sulphuric acid, or of dried chloride of calcium, or of one of these substances in one branch and the other in another. In order that this tube may be used several times, instead of placing above each branch a simple curved tube intended to convey the gases, a tube in which a small globe is blown is adapted to one side. The greatest part of the water is then condensed in the globe, from which it can be expelled at the end of the analysis, and the drying substances retain their power. The apparatus then assumes the form indicated in fig. 39 (page 348). The end which has the bulb is placed in communication with the retort tube by means of a cork.

The apparatus destined to absorb carbonic anhydride is composed of two tubes.

The first, called Liebig's tube, is of the form represented in fig. 40; it contains a highly-concentrated solution of caustic potash. The second is a simple U-shaped tube, one of the branches of which is full

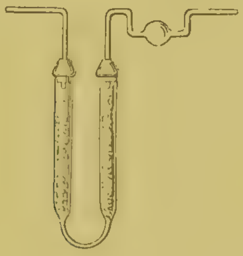
Fig. 39.

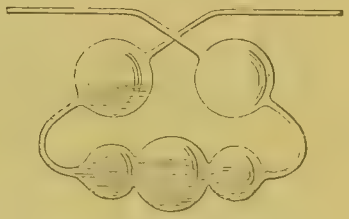
Fig. 40.

of pumice-stone moistened with a solution of caustic potash, while the other contains pieces of caustic potash. This tube should always be fixed in such a manner that the gas shall traverse the pumice-stone before passing over the pieces of potash. Its object is to arrest the small quantity of carbonic anhydride which may have escaped Liebig's tube, and the vapour of water which the gaseous current may have taken from the solution of potash, and which would tend to diminish the weight of the apparatus.

Liebig's tube is joined to the water apparatus and to the tube containing potash by means of india-rubber.

The complete apparatus then has the form represented in our drawing (fig. 41).

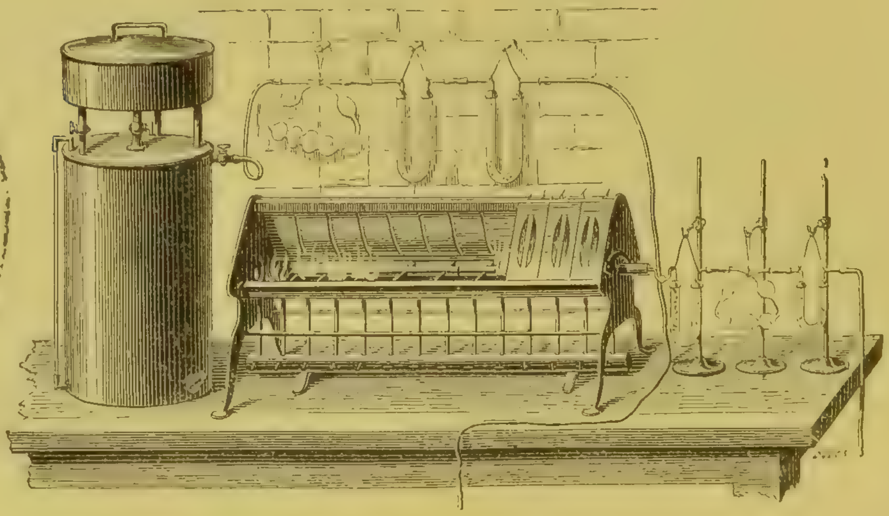
Fig. 41.

Before commencing the analysis, that globe of the Liebig's tube which communicates freely with the interior of the apparatus is gently heated so as to expel a certain quantity of air, and then allowed to cool. A vacuum is made in this globe, and a column of the liquid then rises into it. The level of the liquid in the two globes being thus different, it is necessary to wait a few minutes. If the apparatus leaks at any point, the external air will penetrate into it, the internal pressure again becomes equal to the atmospheric pressure, and the liquid regains its original level in the two globes. If, on the contrary, the apparatus is air-tight, the difference in level remains.

When it is ascertained that the apparatus is air-tight, heat is gradually applied either by means of a gas flame or charcoal, to all that portion of the tube containing pure oxide of copper. When this first part is red hot the fire is gradually brought to the further extremity, until the mixture of oxide of copper and the substance is arrived at. The combustion then commences, and gas bubbles are seen to be disengaged in Liebig's tube. When the current of bubbles slackens, the heat is again advanced, and this continued until the entire length of the tube is heated. When the combustion is terminated, the carbonic anhydride ceases to be disengaged and that which fills the tube is partly absorbed by the solution of potash, the internal pressure diminishes, the liquid rises into one of the side-bulbs of Liebig's tube, and the external air penetrates into the apparatus. The point of the combustion tube is then broken off and placed in communication with a gasometer full of oxygen by means of a long india-rubber tube, and a current of this gas is transmitted into the combustion tube. The oxygen ought first to pass through an apparatus full of caustic potash and chloride of calcium, to free it from the vapour of water it contains, and from carbonic anhydride with which it may be mixed.

The oxygen displaces the carbonic anhydride which filled the tube, and completes the combustion in cases where it is incomplete; moreover, it restores the copper to the state of black oxide, and renders it fit to be used again. We know that the carbonic anhydride has been totally expelled from the retort tube, when the gas which disengages at the end of the apparatus relights a match with a glowing spark at the end of it.

The gaseous current is then arrested, the apparatus dismounted, and a current of air made to pass into the condensing tubes by means of an india-rubber tube. This is to eliminate the oxygen, which, owing to its density being greater than that of air, would give an excess of weight in weighing.

Finally, the U-shaped tube full of chloride of calcium is weighed alone, and the other two tubes together; the excess of these weights over those of the same apparatus before the experiment, gives the weight of the carbonic anhydride and of the water formed. Let P and R be these weights. Knowing that 11 parts of carbonic anhydride contain 3 parts of carbon, and that 9 parts of water contain 1 of hydrogen, we place the proportions:

$$11 : 3 :: P : x; \text{ therefore } x = \frac{3P}{11}.$$

$$9 : 1 :: R : x; \text{ therefore } x = \frac{R}{9}.$$

LEEDS SCHOOL OF MEDICINE

Finally, by two other proportions, the centesimal composition is found.

When chromate of lead is used instead of oxide of copper, the salt being first washed and powdered, the analysis takes place in the same manner.

If the substance to be analyzed be liquid, it is placed in a small thin glass capsule (fig. 42). For this purpose the capsule is gently heated in its widest part, and inverted in the liquid, which rises into the narrow tube terminating the capsule. When a sufficient quantity has entered, the capsule is turned upright, and the narrow part hermetically sealed. The difference between the weights of the capsule when empty and when full gives the weight of the liquid.

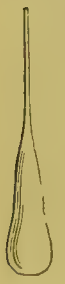
Fig. 42.

The combustion tube is filled in the same way as when acting on a solid; only, instead of placing the substance in it in the manner described, the capsule is thrown into it after its point has been broken, and the tube is then filled with pure oxide of copper.

If the liquid be little volatile, it might be feared that it would only partially decompose, and that a small quantity of unconsumed carbon would remain in the capsule. To obviate this difficulty, a small piece of glass is placed in the tube, and the capsule is thrown in with sufficient force to cause it to be broken in falling, the liquid is then intimately mixed with the oxide of copper, and all loss of carbon is avoided.

If the substance contain chlorine, bromine, iodine, or sulphur, and it be analyzed by means of oxide of copper, a small piece of chromate of lead should be placed in front of this oxide, otherwise volatile chlorides, bromides, or iodides of copper would be produced and added to the water in the weighing, or sulphurous anhydride would be formed and added to the carbonic anhydride. As the chromate of lead transforms these different bodies into chloride, bromide, iodide, or sulphate of lead, and as these latter salts are not volatile, this accident is no longer to be feared.

If the substance contain nitrogen, binoxide of nitrogen will be formed during the combustion. On contact with oxygen this gas is transformed into hyponitric acid, which is deposited either as nitric acid in the tube destined to receive the water, or in the Liebig's tube in the state of alkaline nitrate and nitrite; the analysis is thus vitiated. This cause of error can be remedied by placing metallic copper turnings heated to redness in advance of the oxide of copper. This metal absorbs the oxygen of the binoxide of nitrogen. The gas is thus restored to the state of nitrogen, and can no longer affect the result of the analysis.

M. Piria has introduced a modification in the apparatus we have just described. The combustion tube he uses is open at both ends and divided into two parts by a plug of asbestos. The first part, full of oxide of copper, is kept at red heat. A small vessel containing the substance to be analyzed is placed in the further part, which part is heated after having a current of oxygen passed into it. At the end of the operation the whole tube ought, as usual, to be heated. The substance burns both under the influence of the current of oxygen and of the oxide of copper.

M. Piria also advises that the apparatus should be terminated by an aspirator, which renders the internal pressure weaker than the atmospheric pressure. The carbonic anhydride cannot then permeate the pores of the cork. The atmospheric air, on the contrary, would tend to do this.

In order to show the utility of this precaution, M. Piria demonstrated that in ordinary analyses a portion of the carbonic anhydride is absorbed by the cork, so that if this be placed in a vessel containing lime-water, and the whole put under the receiver of an air-pump, small bubbles of gas which whiten the lime-water are seen to disengage.

2nd. Determination of Nitrogen.—Nitrogen is sometimes determined by volume, sometimes in the state of ammonia. The first of these processes is the more general; the other cannot be applied to compounds containing the nitrile group ($NO^2$).

*Determination of Nitrogen by Volume.*—To find the proportion of nitrogen by volume, a tube is used about 36 inches in length; in the bottom of this tube is placed first a certain quantity of bicarbonate of sodium, then a little pure oxide of copper is put into it, after which there is introduced either the solid substance mixed with a fresh quantity of oxide of copper, or the liquid placed in a capsule. This done, a layer of pure oxide of copper is added, as if an ordinary analysis were to be made, but after this the tube is filled up with copper turnings.

That part which is beyond the copper is drawn out and placed in communication with one of the stop-cocks of a small air-pump by means of caoutchouc, the other stop-cock of the pump is joined also by means of caoutchouc to a bent tube, the vertical portion of which must be at least 32 inches in length, and whose lower portion conducts the gas into a bath of mercury.

Fig. 43 (page 352) represents the apparatus. When arranged, we must, in the first instance, ascertain by means of the air-pump that the stop-cocks and caoutchouc tubes are all air-tight. A small column of mercury is raised in the exit tube, which should maintain its elevation when the pump ceases to be worked.

When satisfied on this point, all the air must be exhausted from the apparatus by the air-pump; then that part of the tube which contains the bicarbonate of sodium is gently heated, causing carbonic anhydride to be disengaged, whereby the pressure is again equalized. The apparatus is again exhausted, and the operation is thus continued until the gas which escapes from the tube while the bicarbonate is being heated is entirely absorbed by a solution of potash.

When the air is entirely eliminated, a graduated glass cylinder, filled with mercury, into the upper part of which a solution of caustic potash has been introduced, is placed over the tube of exit; then that portion of the tube which contains the copper turnings, and that containing the pure oxide of copper, are heated.

When all this part of the tube is red hot, the oxide of copper which is near the carbonate of sodium is heated, and the mixture of oxide of copper and the substance is gradually arrived at, and continuing in this manner, the tube is at last heated throughout its whole length.

The substance is burned as in ordinary analysis. Binoxide of nitrogen is produced, which, on contact with the copper, passes to the state of nitrogen and is collected in the graduated cylinder.

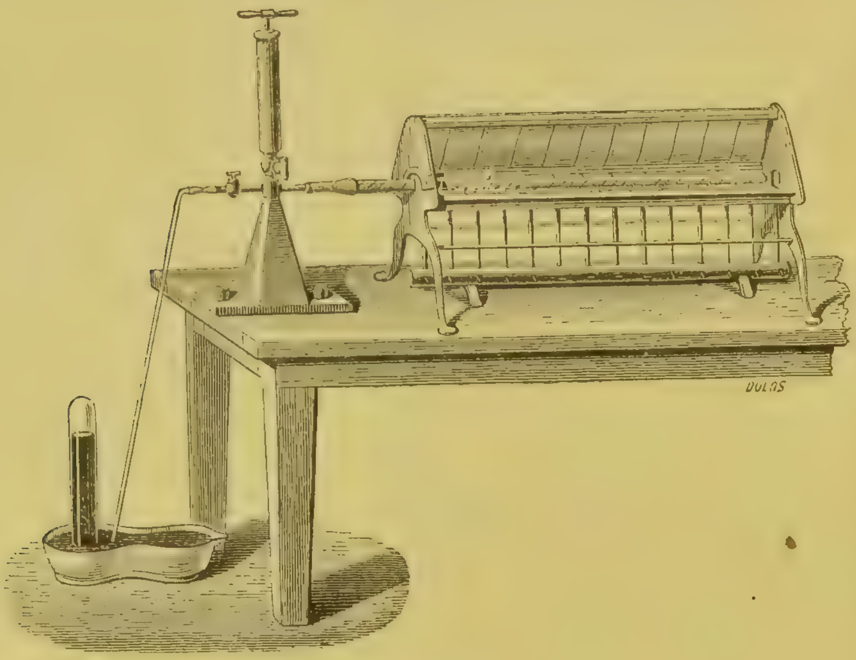

Fig. 43.

When the disengagement of gas ceases, the bicarbonate of sodium is heated in order to produce a disengagement of carbonic anhydride, which drives out the nitrogen contained in the tube.

The operation being concluded, the gas contained in the glass cylinder is measured: this gas consists of pure nitrogen, the carbonic anhydride having been absorbed by the alkaline solution. In order to determine the volume of gas, it is decanted into a graduated tube of small diameter placed over a water bath. The gas is thus saturated with watery vapour, of which it is easy to take account knowing the temperature, and desiccation is therefore unnecesary.

When the gaseous volume is known it must be reduced to the normal pressure and temperature. This is done by employing the following formula, in which $v$ represents the volume observed, and $x$ the volume corrected:

$$x = \frac{v(H - f)}{760(1 + 0{\cdot}00367t)}.$$

Multiplying the corrected volume by 0·0012562, which is the weight in grammes of a cubic centimetre of nitrogen, the weight of the nitrogen collected in the experiment is found, which weight is brought to a per centage by a simple proportion. The letter $f$ in the preceding formula represents the tension of the vapour of water. We give a table of the values of $f$ according to M. Regnault, as well as the values of the denominator $760(1 + 0 \cdot 00367t) = d$ for the temperatures comprised between 0 and 30°.

| *t.* | *d.* | *f.* | *t.* | *d.* | *f.* | *t.* | *d.* | *f.* |
|---|---|---|---|---|---|---|---|---|
| 0° | 760·0 | 4·6 | 11° | 790·7 | 9·8 | 22° | 821·4 | 19·7 |
| 1° | 762·8 | 4·9 | 12° | 793·5 | 10·5 | 23° | 824·1 | 20·9 |
| 2° | 765·6 | 5·3 | 13° | 796·3 | 11·2 | 24° | 826·9 | 22·2 |
| 3° | 768·4 | 5·7 | 14° | 799·1 | 11·9 | 25° | 829·7 | 23·6 |
| 4° | 771·2 | 6·1 | 15° | 801·8 | 12·7 | 26° | 832·5 | 25·0 |
| 5° | 773·9 | 6·5 | 16° | 804·6 | 13·5 | 27° | 835·3 | 26·5 |
| 6° | 776·7 | 7·0 | 17° | 807·4 | 14·4 | 28° | 838·1 | 28·1 |
| 7° | 779·5 | 7·5 | 18° | 810·2 | 15·3 | 29° | 840·9 | 29·8 |
| 8° | 782·3 | 8·0 | 19° | 813·0 | 16·3 | 30° | 843·7 | 31·5 |
| 9° | 785·1 | 8·6 | 20° | 815·8 | 17·4 | | | |
| 10° | 787·9 | 9·2 | 21° | 818·6 | 18·5 | | | |

The analytical process we have just described contains a source of error which must be eliminated. It sometimes happens that a small portion of the binoxide of nitrogen escapes the reducing action of the copper. As this gas only contains half its volume of nitrogen, it is always necessary to ascertain whether there is any in the tube, and in this case to determine its proportion.

After having measured the gas as has been directed, the tube is placed in a vessel containing either a solution of protosulphate of iron or a solution of permanganate of potassium. The binoxide of nitrogen is thereby absorbed. The pure nitrogen which remains is measured, and the difference between the new and the original volume indicates the quantity of binoxide of nitrogen that has disappeared. Then there must be added to the volume of pure nitrogen a volume equal to the half of that of the binoxide, and the calculation is complete.

*Determination of Nitrogen by conversion into Ammonia.*—Messrs. Will and Varrentrapp, to whom we owe this method, recommend the operation to be conducted in the following manner:

Into a retort tube, exactly like that used to determine carbon and hydrogen, a mixture of soda-lime and about 3 decigrammes of the substance is introduced. The tube is then filled with soda-lime, a plug of asbestos is loosely inserted to keep the mixture in the tube, and it is placed in communication, by means of a good cork, with an apparatus

Fig. 44.

with bulbs, as represented in fig. 44 (page 353), the bulbs containing concentrated hydrochloric acid.

The combustion should be conducted as in an ordinary analysis. Under the influence of the soda-lime, the nitrogen of the organic substance is converted into ammonia, which remains in the hydrochloric acid. When gaseous disengagement ceases, the narrow point E of the combustion tube is opened, and air drawn through by means of an india-rubber tube fixed to the open end of the bulb tube. The current of air conveys all the ammoniacal vapours contained in the apparatus into the hydrochloric acid.

This done, the hydrochloric acid in the bulb tube is poured into a small evaporating dish, and the tube is washed with distilled water, and the rinsings added to the hydrochloric acid. An excess of tetrachloride of platinum is then added, and the whole evaporated to dryness in a water-bath. The residue is washed with a mixture of alcohol and ether, then collected on a filter and dried. Finally, it is calcined, and the platinum which remains as residue is weighed. From the weight of this metal that of the nitrogen is deduced: each atom of platinum corresponds to a molecule, or two atoms of nitrogen.

The soda-lime used is obtained by slaking ordinary lime with a solution of soda and calcining the mass in a crucible.

The ammonia may also be collected in a solution of sulphuric acid, and the quantity of this base afterwards determined by a volumetric analysis.

3rd. DETERMINATION OF CHLORINE, BROMINE, AND IODINE.—In order to determine the proportions of these different elements contained in organic substances, these latter are decomposed by pure lime. Chloride, bromide, or iodide of calcium is formed. These salts remain mixed with carbon arising from the organic matter, and with a great excess of lime. When the mass has become cool, it is exhausted by water or by pure nitric acid. The lime is entirely dissolved, as well as the chloride of calcium. It must be filtered to separate the carbon, and when the filter has been well washed, and the water from the washings mixed with the liquid, this is precipitated by means of nitrate of silver; it is boiled to facilitate the collection of the precipitate, and filtered through paper.

When all the precipitate is collected on the filter, this is dried in an oven; then the chloride of silver is carefully separated, thrown into a small porcelain capsule, and melted by means of a spirit-lamp.

Or the filter is folded enclosed by a platinum wire, and entirely burned: the little chloride of silver which adhered is reduced to the state of metallic silver by the hydrogenized gases which form during the combustion.

If the porcelain capsule has been weighed before and after introducing the chloride of silver, the weight of the latter will be known.

Also, if the platinum wire be weighed alone, and then weighed with the ashes of the filter, the difference will be equal to the united weights of the silver and the ashes of the filter; and on deducting the weight of the ashes, determined by a previous experiment, that of the silver is ascertained.

Then the weight of the chloride of silver which gave rise to this metallic silver is calculated, and that of the chloride of silver contained in the capsule added to it; and, finally, the quantity of chlorine corresponding to the weight of silver is also calculated.

The processes are the same with bromine and iodine.

In order to effect the decomposition of the substance by lime, we take a tube 20 inches long and the third of an inch in diameter, close it at one end, and fill it as if an ordinary analysis were to be performed, with the single difference that lime is used instead of oxide of copper.

That part of the tube which contains lime only is first heated, then that containing the mixture of lime and the substance to be analyzed. When the tube has been heated to redness throughout the whole of its length, and maintained for some time at that temperature, it is removed from the fire and allowed to cool.

When the tube is cold, the lime is made to fall gradually into a flask containing a little distilled water, then the interior is washed with dilute nitric acid, which is added to the water in the flask, and the determination is concluded as has been before described.

If the substance in which either the carbon or the chlorine is to be determined were too volatile, the analytical tube should be terminated by a point at one end. A bulb tube should be joined by means of caoutchouc (fig. 45), and its point should be broken after heating the oxide of copper or the lime to redness. In the case of an ordinary analysis, a bulb with two points should be used in order, at the end of the operation, to transmit oxygen through the bulb to cleanse it from the small quantity of carbonic anhydride which may have accumulated there.

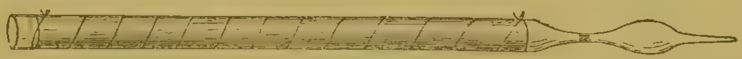
Fig. 45.

4th. Determination of Sulphur, Arsenic, and Phosphorus.—The most simple method of determining these substances consists in transforming sulphur, arsenic, and phosphorus into soluble sulphates, arseniates, and phosphates, which are afterwards determined by the processes used in mineral chemistry.

In order to oxidize the sulphur, phosphorus, and arsenic contained in organic substances, these substances are heated for about twelve hours to 200° with fuming nitric acid, in a hermetically-sealed tube; after opening the tube the acid is saturated by potash, slowly evaporated, and the residue melted in a platinum capsule. The mass when cooled contains the metalloids mentioned as salts in the maximum state of oxidation. If a determination of sulphur has to be made, the solution is then precipitated by chloride of barium and gently heated. The precipitate is collected on a filter, well washed and dried on a stove, then with the filter calcined at red heat in a platinum crucible. As the carbon furnished by the filter reduces a portion of the sulphate of barium to the state of sulphide, the whole must be restored to the state of sulphate : to effect this a little nitric and sulphuric acid is poured on the precipitate, which is then evaporated to dryness. From the weight of the sulphate of barium obtained, less that of the ashes of the filter, the weight of the sulphur contained in the substance analyzed is deduced. When arsenic or phosphorus is to be determined, the solution is precipitated by a mixture of the sulphate of magnesium, chloride of ammonium and ammonia, and the mixture is left for at least 12 hours.

In the case of phosphorus, the precipitate is collected on a filter, then, after drying, it is calcined at a red heat in a porcelain crucible; the double ammoniaco-magnesian salt is transformed into pyrophosphate of magnesium. The weight of the ashes of the filter is deducted from that of the latter compound, and knowing its formula $\left.\begin{matrix}PO'''\\PO'''\\Mg^2\end{matrix}\right\}O^5$, the quantity of phosphorus this salt contains is easily calculated.

If arsenic is to be determined, the double ammoniaco-magnesian salt is collected on a filter weighed after desiccation at 100° ; the filter and the precipitate are then dried at 100° and weighed. On deducting the weight of the filter from the total weight, that of the double salt is found, from which that of the arsenic may be calculated ; it suffices to remember that the formula of this salt is $2\left(\left.\begin{matrix}AsO'''\\Mg''\\NH^4\end{matrix}\right\}O^8\right) + (H^2O)$. If the salt were transformed by calcination into pyro-arseniate of magnesium, operating in the same way as with the phosphate, it would lose 3 or 4 per cent. of arsenic.

5th. DETERMINATION OF METALS.—In order to determine metals, the organic substance must be incinerated. When the pure metal remains, as is the case with gold, platinum, and silver, it only requires to be weighed: when it remains in the state of oxide or carbonate, the quantity is determined by the processes used in mineral analysis, into the description of which the limits of this work will not permit us to enter.

**Eudiometric Analysis.**—Gases may be analyzed by the processes that have been described ; for this purpose we introduce into the combustion-tube an accurately-measured volume of a gas whose density is known ; but when the gases do not contain any other elements besides carbon and hydrogen it is more convenient to determine their composition by means of the eudiometer, which may also be used to determine how much carbon is contained in its oxygenated compounds.

We have already seen in inorganic chemistry that it is possible, by means of the eudiometer, to analyze atmospheric air and the gaseous mixture which results from the decomposition of ammoniacal gas by electricity.

The analysis of the different gaseous compounds met with in organic chemistry presents another difficulty: these gases are not mixtures, but combinations in which the different elements are united and condensed.

Let us take for example the analysis of a gaseous carburetted hydrogen.

A certain volume V of this gas is introduced into the eudiometer, and a volume O of oxygen is added, care being taken that this latter body be in excess, the volume of the gaseous mixture will be $V + O$.

An electric spark is passed into the mixture, the carburetted gas will be burnt, and water and carbonic anhydride will be produced. As the water will be condensed, the gaseous volume remaining will simply consist of carbonic anhydride and the excess of oxygen. This volume, which we will designate by X, is measured, and the carbonic anhydride is then absorbed by means of potash. If, after this absorption, the volume be Y, $X - Y$ will represent the carbonic anhydride absorbed.

The gas remaining will be pure oxygen: to be certain of this, excess of hydrogen should be added and the electric spark transmitted through the mixture, the diminution of volume will indicate the water formed and consequently the oxygen which has disappeared; let Z be the volume of this oxygen.

We know that carbonic anhydride contains a volume of oxygen equal to itself, the oxygen engaged in forming the carbonic anhydride found in the experiment would occupy therefore a volume equal to $X - Y$; if this quantity be added to Z and the sum subtracted from the original volume of oxygen O, the difference will indicate the oxygen consumed to form the water. It will then suffice to double this volume in order to know the proportion of hydrogen contained in the substance.

Knowing the densities of carbonic anhydride, hydrogen, and the substance analyzed, the centesimal composition by weight of this substance can be calculated.

If the substance were oxygenated, still the proportion of carbon it contained could be determined by means of the eudiometer, but that of the hydrogen could not be so determined: this determination would require the knowledge of the oxygen employed, but the quantity of this body contained in the substance is unknown.

Nevertheless, the eudiometric analysis would in this case indicate the presence of oxygen, and by operating as if we had a hydrocarbide, and calculating the composition by weight, we should find quantities of carbon and hydrogen the sum of which would be inferior to the weight of the matter employed.

Substances containing carbon, hydrogen, and nitrogen may be completely analyzed by the eudiometric method.

## VAPOUR DENSITIES.

The vapour density of a body is the proportion existing between the weight of a given volume of its vapour and that of an equal volume of air under the same conditions of pressure and temperature.

Two methods are used to determine vapour densities, that of Gay-Lussac and that of M. Dumas. To this latter must be added the improvement of M. Deville, the object of which is to determine the vapour densities of bodies whose boiling point is very high. This method is especially useful in mineral chemistry. In organic chemistry M. Dumas' method suffices. It enables us to operate up to 500°, which temperature cannot here be used because almost all organic substances decompose before attaining it.

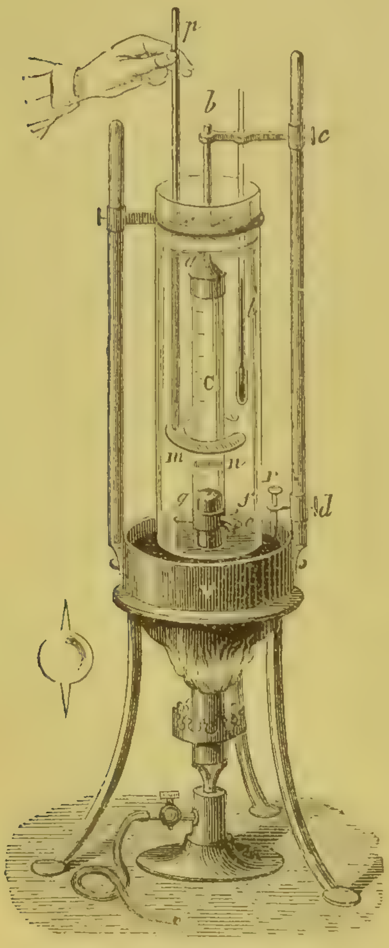

Fig. 46.

Gay-Lussac's Method.—In this process the volume occupied by the vapour of a quantity of liquid, the weight of which has been previously ascertained, is measured. Then the weight of an equal volume of air at the same temperature and pressure is calculated. On dividing the weight of the vapour by that of the air, the density sought for is obtained. The apparatus used is a brass pan (fig. 46), which is placed over a stove after being filled with very dry mercury.

A graduated tube, also filled with dry mercury, is placed over the pan, and round this tube a glass cylinder must be placed, the diameter of which should be two or three inches less than that of the pan, and which, as well as the tube, should be kept in a vertical position by means of iron rods fixed on the handles of the pan. Water is placed in the round space between the tube and the glass cylinder, and a thermometer to indicate the temperature; and one of the iron rods of which we spoke holds at its lower part a needle which shows the outer level of the liquid.

A small vial quite full of the body whose vapour density is to be ascertained is introduced into the tube, after having been weighed first empty and then full, to know the weight of the liquid contained in it. The vial being introduced the mercury is heated; the heat is communicated to the tube and the water in the cylinder: soon the dilatation of the liquid breaks the vial; the liquid is vaporized and presses back the mercury. When the vaporization is completed, and the temperature of the water has reached the point at which the determination is to be made, this temperature is marked, and the volume occupied by the vapour is read on the graduated tube. It is also necessary to ascertain the pressure at which this vapour is found. This pressure is evidently equal to the pressure of the barometer less the mercurial column raised into the tube. In order to know it, we have only to examine what is the external barometric pressure and to measure the column of mercury raised up into the tube.

To take this measure, the lower point of the needle is made to coincide exactly with the level of the mercury; then the vertical distance which separates the upper part of the needle from the level of the mercury in the tube is determined by the cathetometer. On adding the length of the needle, the height of the mercurial column is ascertained.

We have therefore the weight P of a known volume of vapour at a determined pressure and temperature. The weight Q of an equal volume of air, at the same pressure and temperature, is given by the formula

$$Q' = 0{\cdot}0012932 \times \frac{V\,(H-h)}{760\,(1+0{\cdot}00367t)}$$

in which V is the volume of vapour, H the barometric pressure, $h$ the height of the mercury in the tube, and 0·0012932 the weight of a cubic centimetre of air at 0° and under the pressure of $760^{mm}$.

The quotient of P by Q′ is the density sought for.

If we wish to determine a vapour density above 100°, the water of the cylinder must be replaced by oil as transparent as possible, or, what is better, by melted paraffine; but we should then have a source of error in the tension of the mercurial vapour, and it would be better to have recourse to M. Dumas' method. Nevertheless, this cause of error may be avoided by remembering the tension of the vapour of mercury in the calculations. Its varying tensions at different temperatures have been determined with great exactitude by M. Regnault.

Method of M. Dumas.—In the method of Dumas, instead of measuring the volume of vapour produced by a certain weight of the liquid, the weight of the vapour contained in a vessel, the capacity of which is known, is determined. A glass globe is washed, carefully dried, and the neck drawn out in the form represented in fig. 47.

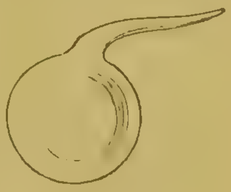
Fig. 47.

Then the globe is weighed and its weight noted, as well as the height of the barometer and the temperature of the balance at the time of the weighing: let P be the weight of the globe, H the height of the barometer, and $t$ the temperature.

Then from 5 to 10 grm. of the substance is introduced into the globe by heating this, and then allowing it to cool after having plunged its point into the liquid: it is then placed in a bath of oil in which it is kept by means of the apparatus represented in fig. 48. The oil-bath being heated to a suitable temperature, the liquid is converted into vapour and passes out by the mouth of the globe, after displacing the atmospheric air, and when the temperature has attained the degree at which it is proposed to determine the vapour density, the heat is regulated so as to maintain a steady temperature; then the point of the globe is closed by means of a blowpipe and the barometric pressure is noted as well as the temperature of the bath. Let A be this pressure and T this temperature.

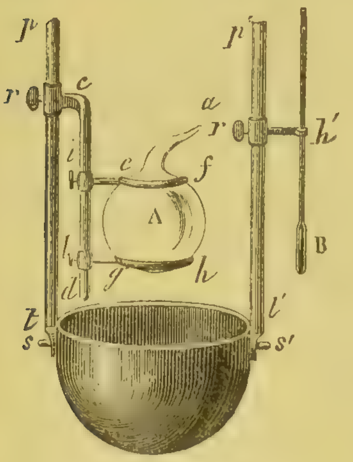

Fig. 48.

The globe is then taken out of the oil, wiped, washed with ether and weighed. Let its weight be B.

The point of the globe is now inserted under mercury and broken. The vapour being condensed a vacuum is produced, and the mercury rises into the globe, which it fills. Then this liquid is poured into a graduated tube, and its volume, which we will call V, is measured.

If all the air were not expelled, that which remains should be collected in a small graduated tube and the volume measured. By means of these different data, the density of the vapour sought for can be ascertained.

The weight P of the globe full of air is equal to that of the glass $\pi$ plus that of the air contained $p$. We have therefore:

$$P = \pi + p.$$

The weight B of the globe in the second weighing is equal to that of the glass $\pi$ plus the weight $x$ of the vapour it contains. We can therefore place the equation:

$$B = \pi + x.$$

From these two equations we get:

$$B - P + p = x.$$

In reality, $B = \pi + x$ and $P = \pi + p$. It is therefore evident that by adding $p$ to $\pi + x$ and $x$ to $\pi + p$, we have the equation $\pi + x + p = \pi + p + x$, or by replacing $\pi + x$ by its value B, and $\pi + p$ by its value P, $B + p = P + x$, from which equation we extract $B - P + p = x$.

This equation indicates that we have only to add the weight of a volume of air equal to the volume of the globe to the difference between the second and the first weighings to have the weight of the vapour. The weight of this volume of air must therefore be calculated.

We know the volume V of the globe at $t°$, the pressure H at which the first weighing was made, and the co-efficient of dilatation of air. We shall then have the weight $p$ of the air contained in the globe by means of the formula :

$$P = \frac{VH}{760\,(1 + 0{\cdot}00367t)} \times 0{\cdot}0012932.$$

The weight of the vapour thus being completely determined, the weight of a volume of air equal to the volume it occupied when the globe was closed must be calculated.

The co-efficient of the glass being designated by K, the volume of the globe at T° will be V (1 + KT) ; not taking account of the difference of temperature between 0 and $t°$, the volume of the vapour will also be V (1 + KT).

This volume, when reduced to normal pressure and temperature, will be :

$$V\,(1 + KT)\,\frac{H'}{760\,(1 + 0{\cdot}00367T)}$$

and the weight of an equal volume of air at the same temperature and pressure :

$$V\,(1 + KT)\,\frac{H'}{760\,(1 + 0{\cdot}00367T)}\,.\,0{\cdot}0012932.$$

The vapour density of the substance is therefore represented by

$$\frac{B - P + \dfrac{VH.0{\cdot}0012932}{760\,(1 + 0{\cdot}00367t)}}{V\,(1 + KT)\,\dfrac{H'0{\cdot}0012932}{760\,(1 + 00367T)}}.$$

Hitherto we have supposed the air to have been completely expelled from the apparatus ; if this were not the case, the experiment would be reduced to the same condition as if a globe had been employed smaller by the volume of air remaining. We will designate this volume by $v$, and the weight corresponding to it by $m$.

We shall have :

$$m = 0{\cdot}0012932.v\,\frac{H''}{760\,(1 + 0{\cdot}00367t'')}$$

Calling the temperature and pressure at the time of measuring the volume $v$, H and $t''$.

The weight of the vapour contained in the globe at the time it is closed is

$$B - P + p - m.$$

On the other hand, the air remaining in the globe would occupy, when this latter has been closed, under the pressure H′ and at the temperature T, a volume represented by

$$v' = v\frac{H''(1 + 0{\cdot}00367t'')}{H'\ (1 + 0{\cdot}00367T)}$$

The volume of vapour ought therefore to be diminished by $v'$ and will be equal to

$$[V(1 + KT) - v']\frac{H'}{760(1 + 0{\cdot}00367T)}$$

As the weight of an equal volume of air under the same conditions of temperature and pressure is

$$[V(1 + KT) - v']\frac{H'}{760(1 + 0{\cdot}00367T)}.0{\cdot}0012932$$

the vapour density sought for will be equal to

$$\frac{B - P + p - m}{0{\cdot}0012932[V(1 + KT) - v']\dfrac{H'}{760(1 + 0{\cdot}00367T)}}$$

The temperature T observed by the mercurial thermometer ought always to be reduced to that given by the air thermometer, or else great mistakes might be committed at high temperatures.

We will give below a table constructed by M. Regnault showing corresponding temperatures of the air and mercurial thermometers.

| Temperatures of the Mercurial Thermometer. | Temperatures of the Air Thermometer corresponding to those of the Mercurial Thermometer when made | |
|---|---|---|
| | of Crystal. | of ordinary Glass. |
| 100 | 100·00 | 100·00 |
| 110 | 109·95 | 110·02 |
| 120 | 119·88 | 120·05 |
| 130 | 129·80 | 130·09 |
| 140 | 139·73 | 140·15 |
| 150 | 149·60 | 150·20 |
| 160 | 159·49 | 160·26 |
| 170 | 169·36 | 170·32 |
| 180 | 179·21 | 180·37 |
| 190 | 189·01 | 190·37 |
| 200 | 198·78 | 200·30 |
| 210 | 208·51 | 210·25 |
| 220 | 218·23 | 220·20 |
| 230 | 227·91 | 230·15 |
| 240 | 237·55 | 240·10 |
| 250 | 247·13 | 249·95 |
| 260 | 256·76 | 259·80 |
| 270 | 266·27 | 269·63 |
| 280 | 275·77 | 269·49 |

M. Deville's Method.—This method, which we cannot describe in detail, and for which we will refer to the original account,* is only that of M. Dumas modified. The modifications consist in the nature of the globe, which is of porcelain instead of glass, and the neck of which is closed by means of the oxyhydrogen blowpipe at the end of the operation.

Moreover, in this process, in order to obtain regular temperatures, the globe is placed in the vapour of a body the boiling point of which is well known and quite fixed. M. Deville has chosen the vapour of mercury, which boils at 350°; of sulphur, which boils at 440°; of cadmium, which boils at 860°; and of zinc, which begins to boil at 1040°. The temperature need not therefore be determined each time, and thus great difficulties are avoided.

When the operation is conducted with mercury or sulphur, glass globes may be used; but with the vapour of cadmium or zinc, porcelain globes are indispensable, because glass becomes exceedingly soft at 860°.

## ORGANIC SERIES.

For a long time organic bodies were classed according to their properties. There were acids, bases, fatty bodies, etc.; later, analogies were discovered between bodies apparently very dissimilar, and a classification into series was adopted. The discoveries of the last ten years have enabled this classification to be systematized, and show how the tetratomicity of carbon may be theoretically deduced.

Carbon is tetratomic, that is to say, it can combine at the maximum with four atoms of hydrogen. The hydrocarbide ($CH^4$) is therefore that which contains the greatest possible quantity of hydrogen. Such a hydrocarbide cannot unite directly with monatomic bodies except by undergoing with them changes of substitution. All the hydrocarbides possessing similar properties are said to be saturated.†

The gas ($CH^4$) is not the only saturated hydrocarbide possible. In reality 2 3, 4, . . . $n$ atoms of carbon can partly saturate each other, and the groups $C^2$, $C^3$, $C^4$, . . . $Cn$, to arrive at the maximum of satura-

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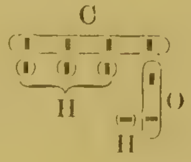
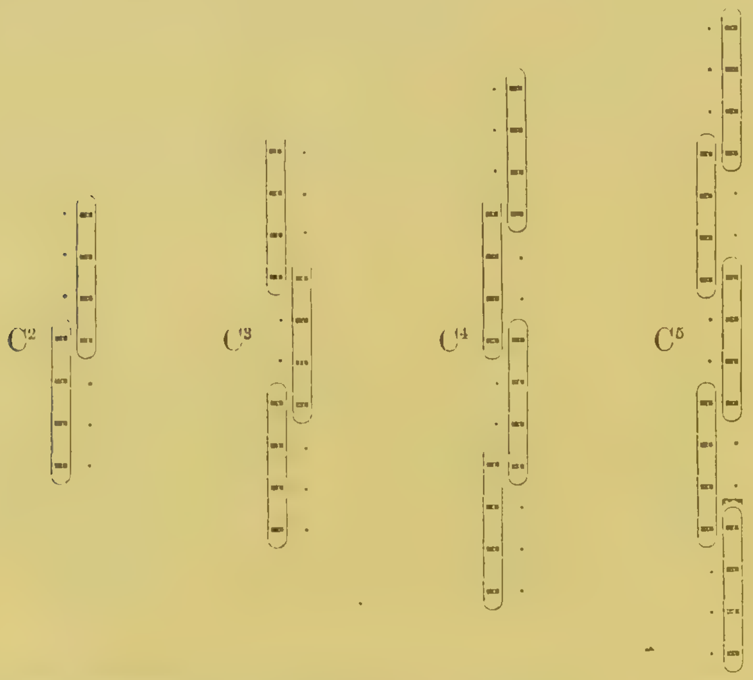
* Annales de Chimie et de Physique, vol. lvii. p. 257.

† Polyatomic radicles may be joined to these hydrocarbides, but this addition is really only a substitution. For instance, a biatomic atom is substituted for a single atom of hydrogen by one of its centres of attraction; its other centre of attraction remains free, and unites with the hydrogen eliminated, as shown in the following figure, in which C represents a tetratomic atom of carbon, O a biatomic atom of oxygen, and H a monatomic atom of hydrogen:



tion, require a smaller number of atoms of hydrogen than would be required by the different atoms which constitute these groups, if they were separate. Two atoms exchange at least two atomicities in order to unite; consequently the group $C^2$ only requires 6H to be saturated. In the group $C^3$ the atomicities lost rise to the number of 4, and the group $C^3$ is only octatomic. In a general way, *n* atoms of carbon lose at the minimum on uniting, a certain number of atomicities which is represented by 2 less than double the number of atoms, as the following figures, in which the groups $C^2$, $C^3$, $C^4$, $C^5$ exchange 2, 4, 6, 8 atomicities, show:



If the atoms of carbon did not lose their capacity of combining when they unite with each other, these groups would require a quantity of hydrogen equal to four times the number of these atoms to be saturated; let it be $4n$. But as they lose a fraction equal to $2n - 2$ of their capacity for saturation, the hydrogen which could saturate them would be $4n - (2n - 2) = 4n - 2n + 2 = 2n + 2$.

The hydrocarbides $CH^4$, $C^2H^6$, $C^3H^8$, $C^4H^{10}$, $C^5H^{12}$, $C^6H^{14}$, $C^7H^{16}$, $C^8H^{18}$, $C^9H^{20}$, $C^{10}H^{22}$, etc., may therefore be considered as saturated; that is to say, as containing the largest possible proportion of hydrogen. The formulæ of these hydrocarbides all differ by the constant quantity $CH^2$:

$$CH^4 + CH^2 = C^2H^6;\ C^2H^6 + CH^2 = C^3H^8, \text{ etc.}$$

Besides, these hydrocarbides have all the same chemical function. Under the same influences they all undergo the same transformations, and regular differences are observed in their physical properties, as a constant difference is observed in their composition. Bodies which have the same chemical functions, and which thus constitute a series, each term of which differs from the preceding by $CH^2$ more, and from the following by $CH^2$ less, have received the name of homologous bodies. The series they form is called an *homologous series*.

We therefore deduce in the first place from the tetratomicity of carbon the existence of an homologous series of saturated hydrocarbides the terms of which correspond to the general formula $C^nH^{2n+2}$.

We know that each saturated compound may successively lose 1, 2, 3, $n$ molecules of the elements it contains, giving rise to non-saturated products.

Each of the hydrocarbides of the preceding series may consequently lose two atoms of hydrogen, producing a new hydrocarbide that is less hydrogenized than its generator.

| | | | | | |
|---|---|---|---|---|---|
| $C\,H^4$ | would therefore give | $C\,H^2$ | $C^7\,H^{16}$ | would give | $C^7\,H^{14}$ |
| $C^2H^6$ | — | $C^2H^4$ | $C^8\,H^{18}$ | — | $C^8\,H^{16}$ |
| $C^3H^8$ | — | $C^3H^6$ | $C^9\,H^{20}$ | — | $C^9\,H^{18}$ |
| $C^4H^{10}$ | — | $C^4H^8$ | $C^{10}H^{22}$ | — | $C^{10}H^{20}$ |
| $C^5H^{12}$ | — | $C^5H^{10}$ | . . . | — | . . . |
| $C^6H^{14}$ | — | $C^6H^{12}$ | . . . | — | . . . |

The hydrocarbides $CH^2$, $C^2H^4$, $C^3H^6$, $C^4H^8$, $C^5H^{10}$, $C^6H^{12}$, $C^7H^{14}$, $C^8H^{16}$, $C^9H^{18}$, $C^{10}H^{20}$, etc., present a relation in their composition similar to that existing between their generators. They are therefore homologous bodies, and their aggregate constitutes a second homologous series, the different terms of which may be expressed by the general formula $C^nH^{2n}$.

The hydrocarbon $CH^2$ cannot lose hydrogen without returning to the state of carbon, but the succeeding hydrocarbides may lose $H^2$ and produce the compounds

$$C^2H^2,\ C^3H^4,\ C^4H^6,\ C^5H^8,\ C^6H^{10},\ C^7H^{12},\ C^8H^{14},\ C^9H^{16},\ C^{10}H^{18},$$

which form a third homologous series expressed by the general formula $C^nH^{2n-2}$.

Continuing to take away hydrogen from the hydrocarbides of the third series, a fourth series would be obtained, and from this a fifth, then a sixth, and so on.

The aggregate of these series forms one vast series which comprises them all. This series of a new order, each term of which is an entire homologous series, has received the name isologous series; it is founded on the characteristic that each of the series it contains has a general expression which differs from that of the preceding homologous series by $H^2$ less, and from the following by $H^2$ more, so that for these general expressions we have:

$$C^nH^{2n+2},\quad C^nH^{2n},\quad C^nH^{2n-2},\quad C^nH^{2n-4},\quad C^nH^{2n-6},\quad C^nH^{2n-8},$$
$$C^nH^{2n-10},\quad C^nH^{2n-12},\ \text{etc.}$$

Each term of an homologous series has the same relations towards

GENERAL TABLE SHOWING THE DIFFERENT SERIES OF HYDROCARBONS.—*See* ORGANIC SERIES, p. 363.

| $\overset{\mathrm{O}}{C^{n}H^{2n+2}}$ | $\overset{\mathrm{II}}{C^{n}H^{2n}}$ | $\overset{\mathrm{O}}{C^{n}H^{2n}}$ | $\overset{\mathrm{IV}}{C^{n}H^{2n-2}}$ | $\overset{\mathrm{II}}{C^{n}H^{2n-2}}$ | $\overset{\mathrm{O}}{C^{n}H^{2n-2}}$ | $\overset{\mathrm{VI}}{C^{n}H^{2n-4}}$ | $\overset{\mathrm{IV}}{C^{n}H^{2n-4}}$ | $\overset{\mathrm{II}}{C^{n}H^{2n-4}}$ | $\overset{\mathrm{O}}{C^{n}H^{2n-4}}$ |
|---|---|---|---|---|---|---|---|---|---|
| $\overset{\mathrm{O}}{C\,H^{4}}$ | $\overset{\mathrm{II}}{C\,H^{2}}$ | | | | | | | | |
| $\overset{\mathrm{O}}{C^{2}H^{6}}$ | $\overset{\mathrm{II}}{C^{2}H^{4}}$ | $\overset{\mathrm{O}}{C^{2}H^{4}}$ | $\overset{\mathrm{IV}}{C^{2}H^{2}}$ | $\overset{\mathrm{II}}{C^{2}H^{2}}$ | $\overset{\mathrm{O}}{C^{2}H^{2}}$ | | | | |
| $\overset{\mathrm{O}}{C^{3}H^{8}}$ | $\overset{\mathrm{II}}{C^{3}H^{6}}$ | $\overset{\mathrm{O}}{C^{3}H^{6}}$ | $\overset{\mathrm{IV}}{C^{3}H^{4}}$ | $\overset{\mathrm{II}}{C^{3}H^{4}}$ | $\overset{\mathrm{O}}{C^{3}H^{4}}$ | $\overset{\mathrm{VI}}{C^{3}H^{2}}$ | $\overset{\mathrm{IV}}{C^{3}H^{2}}$ | $\overset{\mathrm{II}}{C^{3}H^{2}}$ | $\overset{\mathrm{O}}{C^{3}H^{2}}$ |
| $\overset{\mathrm{O}}{C^{4}H^{10}}$ | $\overset{\mathrm{II}}{C^{4}H^{8}}$ | $\overset{\mathrm{O}}{C^{4}H^{8}}$ | $\overset{\mathrm{IV}}{C^{4}H^{6}}$ | $\overset{\mathrm{II}}{C^{4}H^{6}}$ | $\overset{\mathrm{O}}{C^{4}H^{6}}$ | $\overset{\mathrm{VI}}{C^{4}H^{4}}$ | $\overset{\mathrm{IV}}{C^{4}H^{4}}$ | $\overset{\mathrm{II}}{C^{4}H^{4}}$ | $\overset{\mathrm{O}}{C^{4}H^{4}}$ |
| $\overset{\mathrm{O}}{C^{5}H^{12}}$ | $\overset{\mathrm{II}}{C^{5}H^{10}}$ | $\overset{\mathrm{O}}{C^{5}H^{10}}$ | $\overset{\mathrm{IV}}{C^{5}H^{8}}$ | $\overset{\mathrm{II}}{C^{5}H^{8}}$ | $\overset{\mathrm{O}}{C^{5}H^{8}}$ | $\overset{\mathrm{VI}}{C^{5}H^{6}}$ | $\overset{\mathrm{IV}}{C^{5}H^{6}}$ | $\overset{\mathrm{II}}{C^{5}H^{6}}$ | $\overset{\mathrm{O}}{C^{5}H^{6}}$ |
| $\overset{\mathrm{O}}{C^{6}H^{14}}$ | $\overset{\mathrm{II}}{C^{6}H^{12}}$ | $\overset{\mathrm{O}}{C^{6}H^{12}}$ | $\overset{\mathrm{IV}}{C^{6}H^{10}}$ | $\overset{\mathrm{II}}{C^{6}H^{10}}$ | $\overset{\mathrm{O}}{C^{6}H^{10}}$ | $\overset{\mathrm{VI}}{C^{6}H^{8}}$ | $\overset{\mathrm{IV}}{C^{6}H^{8}}$ | $\overset{\mathrm{II}}{C^{6}H^{8}}$ | $\overset{\mathrm{O}}{C^{6}H^{8}}$ |
| $\overset{\mathrm{O}}{C^{7}H^{16}}$ | $\overset{\mathrm{II}}{C^{7}H^{14}}$ | $\overset{\mathrm{O}}{C^{7}H^{14}}$ | $\overset{\mathrm{IV}}{C^{7}H^{12}}$ | $\overset{\mathrm{II}}{C^{7}H^{12}}$ | $\overset{\mathrm{O}}{C^{7}H^{12}}$ | $\overset{\mathrm{VI}}{C^{7}H^{10}}$ | $\overset{\mathrm{VI}}{C^{7}H^{10}}$ | $\overset{\mathrm{II}}{C^{7}H^{10}}$ | $\overset{\mathrm{O}}{C^{7}H^{10}}$ |
| $\overset{\mathrm{O}}{C^{8}H^{18}}$ | $\overset{\mathrm{II}}{C^{8}H^{16}}$ | $\overset{\mathrm{O}}{C^{8}H^{16}}$ | $\overset{\mathrm{IV}}{C^{8}H^{14}}$ | $\overset{\mathrm{II}}{C^{8}H^{14}}$ | $\overset{\mathrm{O}}{C^{8}H^{14}}$ | $\overset{\mathrm{VI}}{C^{8}H^{12}}$ | $\overset{\mathrm{IV}}{C^{8}H^{12}}$ | $\overset{\mathrm{II}}{C^{8}H^{12}}$ | $\overset{\mathrm{O}}{C^{8}H^{12}}$ |
| $\overset{\mathrm{O}}{C^{9}H^{20}}$ | $\overset{\mathrm{II}}{C^{9}H^{18}}$ | $\overset{\mathrm{O}}{C^{9}H^{18}}$ | $\overset{\mathrm{IV}}{C^{9}H^{16}}$ | $\overset{\mathrm{II}}{C^{9}H^{16}}$ | $\overset{\mathrm{O}}{C^{9}H^{16}}$ | $\overset{\mathrm{VI}}{C^{9}H^{14}}$ | $\overset{\mathrm{IV}}{C^{9}H^{14}}$ | $\overset{\mathrm{II}}{C^{9}H^{14}}$ | $\overset{\mathrm{O}}{C^{9}H^{14}}$ |
| $\overset{\mathrm{O}}{C^{10}H^{22}}$ | $\overset{\mathrm{II}}{C^{10}H^{20}}$ | $\overset{\mathrm{O}}{C^{10}H^{20}}$ | $\overset{\mathrm{IV}}{C^{10}H^{18}}$ | $\overset{\mathrm{II}}{C^{10}H^{18}}$ | $\overset{\mathrm{O}}{C^{10}H^{18}}$ | $\overset{\mathrm{VI}}{C^{10}H^{16}}$ | $\overset{\mathrm{IV}}{C^{10}H^{16}}$ | $\overset{\mathrm{II}}{C^{10}H^{16}}$ | $\overset{\mathrm{O}}{C^{10}H^{16}}$ |
| $\overset{\mathrm{O}}{C^{11}H^{24}}$ | $\overset{\mathrm{II}}{C^{11}H^{22}}$ | $\overset{\mathrm{O}}{C^{11}H^{22}}$ | $\overset{\mathrm{IV}}{C^{11}H^{20}}$ | $\overset{\mathrm{II}}{C^{11}H^{20}}$ | $\overset{\mathrm{O}}{C^{11}H^{20}}$ | $\overset{\mathrm{VI}}{C^{11}H^{18}}$ | $\overset{\mathrm{IV}}{C^{11}H^{18}}$ | $\overset{\mathrm{II}}{C^{11}H^{18}}$ | $\overset{\mathrm{O}}{C^{11}H^{18}}$ |
| $\overset{\mathrm{O}}{C^{12}H^{26}}$ | $\overset{\mathrm{II}}{C^{12}H^{24}}$ | $\overset{\mathrm{O}}{C^{12}H^{24}}$ | $\overset{\mathrm{IV}}{C^{12}H^{22}}$ | $\overset{\mathrm{II}}{C^{12}H^{22}}$ | $\overset{\mathrm{O}}{C^{12}H^{22}}$ | $\overset{\mathrm{VI}}{C^{12}H^{20}}$ | $\overset{\mathrm{IV}}{C^{12}H^{20}}$ | $\overset{\mathrm{II}}{C^{12}H^{20}}$ | $\overset{\mathrm{O}}{C^{12}H^{20}}$ |
| $\overset{\mathrm{O}}{C^{13}H^{28}}$ | $\overset{\mathrm{II}}{C^{13}H^{26}}$ | $\overset{\mathrm{O}}{C^{13}H^{26}}$ | $\overset{\mathrm{IV}}{C^{13}H^{24}}$ | $\overset{\mathrm{II}}{C^{13}H^{24}}$ | $\overset{\mathrm{O}}{C^{13}H^{24}}$ | $\overset{\mathrm{VI}}{C^{13}H^{22}}$ | $\overset{\mathrm{IV}}{C^{13}H^{22}}$ | $\overset{\mathrm{II}}{C^{13}H^{22}}$ | $\overset{\mathrm{O}}{C^{13}H^{22}}$ |

GENERAL TABLE SHOWING THE DIFFERENT SERIES OF HYDROCARBONS.—*continued.*

| $C^nH^{2n-6}{}^{\mathrm{VIII}}$ | $C^nH^{2n-6}{}^{\mathrm{VI}}$ | $C^nH^{2n-6}{}^{\mathrm{IV}}$ | $C^nH^{2n-6}{}^{\mathrm{II}}$ | $C^nH^{2n-6}{}^{0}$ | $C^nH^{2n-8}{}^{\mathrm{X}}$ | $C^nH^{2n-8}{}^{\mathrm{VIII}}$ | $C^nH^{2n-8}{}^{\mathrm{VI}}$ | $C^nH^{2n-8}{}^{\mathrm{IV}}$ | $C^nH^{2n-8}{}^{\mathrm{II}}$ | $C^nH^{2n-8}{}^{0}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| $C^4H^2{}^{\mathrm{VIII}}$ | $C^4H^2{}^{\mathrm{VI}}$ | $C^4H^2{}^{\mathrm{IV}}$ | $C^4H^2{}^{\mathrm{II}}$ | $C^4H^2{}^{0}$ | .. | .. | .. | .. | .. | .. |
| $C^5H^4{}^{\mathrm{VIII}}$ | $C^5H^4{}^{\mathrm{VI}}$ | $C^5H^4{}^{\mathrm{IV}}$ | $C^5H^4{}^{\mathrm{II}}$ | $C^5H^4{}^{0}$ | $C^5H^2{}^{\mathrm{X}}$ | $C^5H^2{}^{\mathrm{VIII}}$ | $C^5H^2{}^{\mathrm{VI}}$ | $C^5H^2{}^{\mathrm{IV}}$ | $C^5H^2{}^{\mathrm{II}}$ | $C^5H^2{}^{0}$ |
| $C^6H^6{}^{\mathrm{VIII}}$ | $C^6H^6{}^{\mathrm{VI}}$ | $C^6H^6{}^{\mathrm{IV}}$ | $C^6H^6{}^{\mathrm{II}}$ | $C^6H^6{}^{0}$ | $C^6H^4{}^{\mathrm{X}}$ | $C^6H^4{}^{\mathrm{VIII}}$ | $C^6H^4{}^{\mathrm{VI}}$ | $C^6H^4{}^{\mathrm{IV}}$ | $C^6H^4{}^{\mathrm{II}}$ | $C^6H^4{}^{0}$ |
| $C^7H^8{}^{\mathrm{VIII}}$ | $C^7H^8{}^{\mathrm{VI}}$ | $C^7H^8{}^{\mathrm{IV}}$ | $C^7H^8{}^{\mathrm{II}}$ | $C^7H^8{}^{0}$ | $C^7H^6{}^{\mathrm{X}}$ | $C^7H^6{}^{\mathrm{VIII}}$ | $C^7H^6{}^{\mathrm{VI}}$ | $C^7H^6{}^{\mathrm{IV}}$ | $C^7H^6{}^{\mathrm{II}}$ | $C^7H^6{}^{0}$ |
| $C^8H^{10}{}^{\mathrm{VIII}}$ | $C^8H^{10}{}^{\mathrm{VI}}$ | $C^8H^{10}{}^{\mathrm{IV}}$ | $C^8H^{10}{}^{\mathrm{II}}$ | $C^8H^{10}{}^{0}$ | $C^8H^8{}^{\mathrm{X}}$ | $C^8H^8{}^{\mathrm{VIII}}$ | $C^8H^8{}^{\mathrm{VI}}$ | $C^8H^8{}^{\mathrm{IV}}$ | $C^8H^8{}^{\mathrm{II}}$ | $C^8H^8{}^{0}$ |
| $C^9H^{12}{}^{\mathrm{VIII}}$ | $C^9H^{12}{}^{\mathrm{VI}}$ | $C^9H^{12}{}^{\mathrm{IV}}$ | $C^9H^{12}{}^{\mathrm{II}}$ | $C^9H^{12}{}^{0}$ | $C^9H^{10}{}^{\mathrm{X}}$ | $C^9H^{10}{}^{\mathrm{VIII}}$ | $C^9H^{10}{}^{\mathrm{VI}}$ | $C^9H^{10}{}^{\mathrm{IV}}$ | $C^9H^{10}{}^{\mathrm{II}}$ | $C^9H^{10}{}^{0}$ |
| $C^{10}H^{14}{}^{\mathrm{VIII}}$ | $C^{10}H^{14}{}^{\mathrm{VI}}$ | $C^{10}H^{14}{}^{\mathrm{IV}}$ | $C^{10}H^{14}{}^{\mathrm{II}}$ | $C^{10}H^{14}{}^{0}$ | $C^{10}H^{12}{}^{\mathrm{X}}$ | $C^{10}H^{12}{}^{\mathrm{VIII}}$ | $C^{10}H^{12}{}^{\mathrm{VI}}$ | $C^{10}H^{12}{}^{\mathrm{IV}}$ | $C^{10}H^{12}{}^{\mathrm{II}}$ | $C^{10}H^{12}{}^{0}$ |
| $C^{11}H^{16}{}^{\mathrm{VIII}}$ | $C^{11}H^{16}{}^{\mathrm{VI}}$ | $C^{11}H^{16}{}^{\mathrm{IV}}$ | $C^{11}H^{16}{}^{\mathrm{II}}$ | $C^{11}H^{16}{}^{0}$ | $C^{11}H^{14}{}^{\mathrm{X}}$ | $C^{11}H^{14}{}^{\mathrm{VIII}}$ | $C^{11}H^{14}{}^{\mathrm{VI}}$ | $C^{11}H^{14}{}^{\mathrm{IV}}$ | $C^{11}H^{14}{}^{\mathrm{II}}$ | $C^{11}H^{14}{}^{0}$ |
| $C^{12}H^{18}{}^{\mathrm{VIII}}$ | $C^{12}H^{18}{}^{\mathrm{VI}}$ | $C^{12}H^{18}{}^{\mathrm{IV}}$ | $C^{12}H^{18}{}^{\mathrm{II}}$ | $C^{12}H^{18}{}^{0}$ | $C^{12}H^{16}{}^{\mathrm{X}}$ | $C^{12}H^{16}{}^{\mathrm{VIII}}$ | $C^{12}H^{16}{}^{\mathrm{VI}}$ | $C^{12}H^{16}{}^{\mathrm{IV}}$ | $C^{12}H^{16}{}^{\mathrm{II}}$ | $C^{12}H^{16}{}^{0}$ |
| $C^{13}H^{20}{}^{\mathrm{VIII}}$ | $C^{13}H^{20}{}^{\mathrm{VI}}$ | $C^{13}H^{20}{}^{\mathrm{IV}}$ | $C^{13}H^{20}{}^{\mathrm{II}}$ | $C^{13}H^{20}{}^{0}$ | $C^{13}H^{18}{}^{\mathrm{X}}$ | $C^{13}H^{18}{}^{\mathrm{VIII}}$ | $C^{13}H^{18}{}^{\mathrm{VI}}$ | $C^{13}H^{18}{}^{\mathrm{IV}}$ | $C^{13}H^{18}{}^{\mathrm{II}}$ | $C^{13}H^{18}{}^{0}$ |

## GENERAL TABLE SHOWING THE DIFFERENT SERIES OF HYDROCARBONS.—*continued.*

| $\overset{\text{XII}}{C^{n}H^{2n-10}}$ | $\overset{\text{X}}{C^{n}H^{2n-10}}$ | $\overset{\text{VIII}}{C^{n}H^{2n-10}}$ | $\overset{\text{VI}}{C^{n}H^{2n-10}}$ | $\overset{\text{IV}}{C^{n}H^{2n-10}}$ | $\overset{\text{II}}{C^{n}H^{2n-10}}$ | $\overset{\text{O}}{C^{n}H^{2n-10}}$ |
|---|---|---|---|---|---|---|
| .. | .. | .. | .. | .. | .. | .. |
| .. | .. | .. | .. | .. | .. | .. |
| .. | .. | .. | .. | .. | .. | .. |
| .. | .. | .. | .. | .. | .. | .. |
| .. | .. | .. | .. | .. | .. | .. |
| $\overset{\text{XII}}{C^{6}H^{2}}$ | $\overset{\text{X}}{C^{6}H^{2}}$ | $\overset{\text{VIII}}{C^{6}H^{2}}$ | $\overset{\text{VI}}{C^{6}H^{2}}$ | $\overset{\text{IV}}{C^{6}H^{2}}$ | $\overset{\text{II}}{C^{6}H^{2}}$ | $\overset{\text{O}}{C^{6}H^{2}}$ |
| $\overset{\text{XII}}{C^{7}H^{4}}$ | $\overset{\text{X}}{C^{7}H^{4}}$ | $\overset{\text{VIII}}{C^{7}H^{4}}$ | $\overset{\text{VI}}{C^{7}H^{4}}$ | $\overset{\text{IV}}{C^{7}H^{4}}$ | $\overset{\text{II}}{C^{7}H^{4}}$ | $\overset{\text{O}}{C^{7}H^{4}}$ |
| $\overset{\text{XII}}{C^{8}H^{6}}$ | $\overset{\text{X}}{C^{8}H^{6}}$ | $\overset{\text{VIII}}{C^{8}H^{6}}$ | $\overset{\text{VI}}{C^{8}H^{6}}$ | $\overset{\text{IV}}{C^{8}H^{6}}$ | $\overset{\text{II}}{C^{8}H^{6}}$ | $\overset{\text{O}}{C^{8}H^{6}}$ |
| $\overset{\text{XII}}{C^{9}H^{8}}$ | $\overset{\text{X}}{C^{9}H^{8}}$ | $\overset{\text{VIII}}{C^{9}H^{8}}$ | $\overset{\text{VI}}{C^{9}H^{8}}$ | $\overset{\text{IV}}{C^{9}H^{8}}$ | $\overset{\text{II}}{C^{9}H^{8}}$ | $\overset{\text{O}}{C^{9}H^{8}}$ |
| $\overset{\text{XII}}{C^{10}H^{10}}$ | $\overset{\text{X}}{C^{10}H^{10}}$ | $\overset{\text{VIII}}{C^{10}H^{10}}$ | $\overset{\text{VI}}{C^{10}H^{10}}$ | $\overset{\text{IV}}{C^{10}H^{10}}$ | $\overset{\text{II}}{C^{10}H^{10}}$ | $\overset{\text{O}}{C^{10}H^{10}}$ |
| $\overset{\text{XII}}{C^{11}H^{12}}$ | $\overset{\text{X}}{C^{11}H^{12}}$ | $\overset{\text{VIII}}{C^{11}H^{12}}$ | $\overset{\text{VI}}{C^{11}H^{12}}$ | $\overset{\text{IV}}{C^{11}H^{12}}$ | $\overset{\text{II}}{C^{11}H^{12}}$ | $\overset{\text{O}}{C^{11}H^{12}}$ |
| $\overset{\text{XII}}{C^{12}H^{14}}$ | $\overset{\text{X}}{C^{12}H^{14}}$ | $\overset{\text{VIII}}{C^{12}H^{14}}$ | $\overset{\text{VI}}{C^{12}H^{14}}$ | $\overset{\text{IV}}{C^{12}H^{14}}$ | $\overset{\text{II}}{C^{12}H^{14}}$ | $\overset{\text{O}}{C^{12}H^{14}}$ |
| $\overset{\text{XII}}{C^{13}H^{16}}$ | $\overset{\text{X}}{C^{13}H^{16}}$ | $\overset{\text{VIII}}{C^{13}H^{16}}$ | $\overset{\text{VI}}{C^{13}H^{16}}$ | $\overset{\text{IV}}{C^{13}H^{16}}$ | $\overset{\text{II}}{C^{13}H^{16}}$ | $\overset{\text{O}}{C^{13}H^{16}}$ |

## GENERAL TABLE SHOWING THE DIFFERENT SERIES OF HYDROCARBONS—*continued.*

| $\overset{\text{XIV}}{C^{n}H^{2n-12}}$ | $\overset{\text{XII}}{C^{n}H^{2n-12}}$ | $\overset{\text{X}}{C^{n}H^{2n-12}}$ | $\overset{\text{VIII}}{C^{n}H^{2n-12}}$ | $\overset{\text{VI}}{C^{n}H^{2n-12}}$ | $\overset{\text{IV}}{C^{n}H^{2n-12}}$ | $\overset{\text{II}}{C^{n}H^{2n-12}}$ | $\overset{\text{O}}{C^{n}H^{2n-12}}$ |
|---|---|---|---|---|---|---|---|
| .. | .. | .. | .. | .. | .. | .. | .. |
| .. | .. | .. | .. | .. | .. | .. | .. |
| .. | .. | .. | .. | .. | .. | .. | .. |
| .. | .. | .. | .. | .. | .. | .. | .. |
| .. | .. | .. | .. | .. | .. | .. | .. |
| .. | .. | .. | .. | .. | .. | .. | .. |
| $\overset{\text{XIV}}{C^{7}H^{2}}$ | $\overset{\text{XII}}{C^{7}H^{2}}$ | $\overset{\text{X}}{C^{7}H^{2}}$ | $\overset{\text{VIII}}{C^{7}H^{2}}$ | $\overset{\text{VI}}{C^{7}H^{2}}$ | $\overset{\text{IV}}{C^{7}H^{2}}$ | $\overset{\text{II}}{C^{7}H^{2}}$ | $\overset{\text{O}}{C^{7}H^{2}}$ |
| $\overset{\text{XIV}}{C^{8}H^{4}}$ | $\overset{\text{XII}}{C^{8}H^{4}}$ | $\overset{\text{X}}{C^{8}H^{4}}$ | $\overset{\text{VIII}}{C^{8}H^{4}}$ | $\overset{\text{VI}}{C^{8}H^{4}}$ | $\overset{\text{IV}}{C^{8}H^{4}}$ | $\overset{\text{II}}{C^{8}H^{4}}$ | $\overset{\text{O}}{C^{8}H^{4}}$ |
| $\overset{\text{XIV}}{C^{9}H^{6}}$ | $\overset{\text{XII}}{C^{9}H^{6}}$ | $\overset{\text{X}}{C^{9}H^{6}}$ | $\overset{\text{VIII}}{C^{9}H^{6}}$ | $\overset{\text{VI}}{C^{9}H^{6}}$ | $\overset{\text{IV}}{C^{9}H^{6}}$ | $\overset{\text{II}}{C^{9}H^{6}}$ | $\overset{\text{O}}{C^{9}H^{6}}$ |
| $\overset{\text{XIV}}{C^{10}H^{8}}$ | $\overset{\text{XII}}{C^{10}H^{8}}$ | $\overset{\text{X}}{C^{10}H^{8}}$ | $\overset{\text{VIII}}{C^{10}H^{8}}$ | $\overset{\text{VI}}{C^{10}H^{8}}$ | $\overset{\text{IV}}{C^{10}H^{8}}$ | $\overset{\text{II}}{C^{10}H^{8}}$ | $\overset{\text{O}}{C^{10}H^{8}}$ |
| $\overset{\text{XIV}}{C^{11}H^{10}}$ | $\overset{\text{XII}}{C^{11}H^{10}}$ | $\overset{\text{X}}{C^{11}H^{10}}$ | $\overset{\text{VIII}}{C^{11}H^{10}}$ | $\overset{\text{VI}}{C^{11}H^{10}}$ | $\overset{\text{IV}}{C^{11}H^{10}}$ | $\overset{\text{II}}{C^{11}H^{10}}$ | $\overset{\text{O}}{C^{11}H^{10}}$ |
| $\overset{\text{XIV}}{C^{12}H^{12}}$ | $\overset{\text{XII}}{C^{12}H^{12}}$ | $\overset{\text{X}}{C^{12}H^{12}}$ | $\overset{\text{VIII}}{C^{12}H^{12}}$ | $\overset{\text{VI}}{C^{12}H^{12}}$ | $\overset{\text{IV}}{C^{12}H^{12}}$ | $\overset{\text{II}}{C^{12}H^{12}}$ | $\overset{\text{O}}{C^{12}H^{12}}$ |
| $\overset{\text{XIV}}{C^{13}H^{14}}$ | $\overset{\text{XII}}{C^{13}H^{14}}$ | $\overset{\text{X}}{C^{13}H^{14}}$ | $\overset{\text{VIII}}{C^{13}H^{14}}$ | $\overset{\text{VI}}{C^{13}H^{14}}$ | $\overset{\text{IV}}{C^{13}H^{14}}$ | $\overset{\text{II}}{C^{13}H^{14}}$ | $\overset{\text{O}}{C^{13}H^{14}}$ |

the corresponding term of the other homologous series as is shown between the general expressions of these series, that is to say, they differ between themselves by one or more times $H^2$ more or less. Bodies presenting these relations are called isologous.

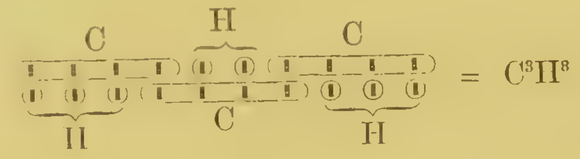
So far we have supposed that each homologous series is simple, that is to say, that each of the preceding formulæ applies to a single hydrocarbide. Nevertheless, facts show that this is not the case.

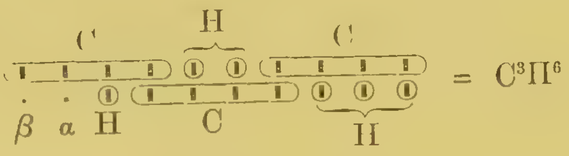
In the preceding explanations it has been shown how a number of other non-saturated hydrocarbides correspond to each saturated hydrocarbide answering to the formula $C^nH^{2n+2}$, and these non-saturated hydrocarbides ought, according to their relations with the first, to act as bi, tri, tetra, . . . . hexatomic radicles.

Let us consider the saturated series $C^nH^{2n+2}$ and the next to it the series $C^nH^{2n}$, and for simplicity let us in these series take two hydrocarbides containing the same quantity of carbon, such as the compounds $(C^3H^8)$ and $(C^3H^6)$.

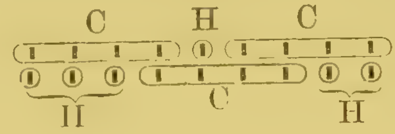
It is clear that $(C^3H^6)$ has a constitution analogous to $(C^3H^8)$, with the slight difference that two of the atoms of hydrogen are absent, and consequently leave two centres of attraction vacant. The following figures show these relations:

EDS
OOL OF
DICIN





The letters C indicate the atoms of carbon, H the hydrogen, and the Greek letters α and β the free centres of attraction in the hydrocarbide $(C^3H^6)$. But it would be equally possible that the three atoms of carbon which enter into the constitution of the compound $(C^3H^6)$ should in the above graphic representation overlap one another more and should lose more than four atomicities, this figure four only expressing the minimum quantity they could lose. For instance, it will readily be understood that the body $(C^3H^6)$ might have the following form:



in which no free centre of attraction would be found.

Thus theory indicates that there may be two isomeric hydrocarbides corresponding to the formula $(C^3H^6)$, one of which is saturated, and the other derived from the hydrocarbide $(C^3H^8)$ acting as a biatomic radicle.

The reasoning which we have applied to the body ($C^3H^6$) being equally applicable to all its homologues, we may say that while each term is simple, considered with regard to saturation, in the $C^nH^{2n+2}$ series, it is possible that each term may be double in the $C^nH^{2n}$ series.

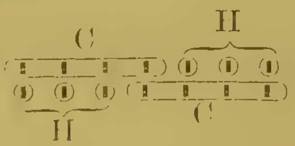
If the same reasoning were applied to the $C^nH^{2n-2}$ series, it would be found that three isomers are possible for each term; one derived from the corresponding term of the first series by eliminating $H^4$, and which acts as a tetratomic radicle; the second acting as a biatomic radicle, derived from the corresponding saturated term of the second series; and the third saturated.

For the fourth series, four isomers of each term will similarly be found; for the fifth, five; and generally for any series whatever, a number of isomers equal to the number which represents the number of the order of the series, will be found.

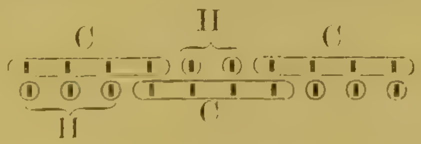
The general view of the hydrocarbides classed in series then assumes the form represented in the table. In this table the atomicity of radicles is indicated by dashes or Roman figures, and the sign o indicates saturation.

The isomers which arise from differences of saturation, and which are indicated in this table, are very far from being the only ones possible; each hydrocarbide, whether saturated or not, may have isomers of the same degree of saturation as itself, and in greater number in proportion as it contains more carbon. These isomers are owing to the atoms of carbon being capable of being grouped in different ways, in order to exchange a certain number of atomicities among themselves.

If we take the hydrocarbides ($CH^4$), ($C^2H^6$), and ($C^3H^8$), we shall see that they cannot have isomers. The first contains a single atom of carbon, and the other two contain too few for different groupings to be produced. Between two atoms of carbon, which only exchange one atomicity, it is evident that there can only be the grouping



When the atoms of carbon are increased in number to three, they may be imagined as united in the following manner:



in which one of the three atoms loses two atomicities, and the two others one each, unless they overlap each other more and give a hydrocarbide less hydrogenized than ($C^3H^8$).

But if the hydrocarbide ($C^4H^{10}$) be considered, it will be found that it can have two isomers. In reality the condition under which this hydrocarbide exists is that the four atoms of carbon lose a total of six atomicities. This condition may be fulfilled in two different ways :

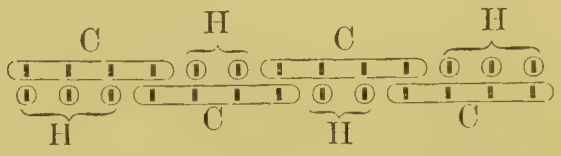


Fig. *a*.

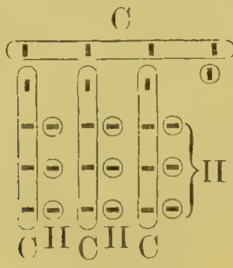
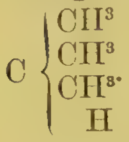


Fig. *β*.

Either, as in the figure *a*, the four atoms form a chain in which the two middle atoms each lose two atomicities, while those at the extremities only lose one.

Or, as in figure *β*, one atom of carbon exchanges three atomicities with three other atoms of the same body which only themselves exchange one each, thence the two isomeric hydrocarbides $C^4H^{10}$ and



$$C\left\{\begin{array}{l}CH^3\\CH^3\\CH^3\\H\end{array}\right.$$

For analogous reasons, it will be found that three isomers are possible for the hydrocarbide ($C^5H^{12}$), four for the hydrocarbide ($C^6H^{14}$), and so on.

Thus, starting from the atomicity of carbon, we may deduce what are the hydrocarbides which exist, or at least which may be admitted theoretically, and all these hydrocarbides may be classed in homologous series, united among themselves, and forming one vast isologous series which includes them all.

If we now examine what ought to be the properties of the saturated hydrocarbides of the different series, we shall be convinced that by losing 1, 2, 3, . . . *n* atoms of hydrogen, these compounds might produce mono, bi, tri . . . *n* atomic radicles. Among these radicles, those of uneven atomicity are merely the non-saturated hydrocarbides indicated in the table. The radicles of even atomicity do not appear there because they cannot exist in a free state.

I will suppose that the monatomic radicle $C^8H^{17}$, the biatomic radicle $C^8H^{16}$, the triatomic radicle $C^8H^{15}$, the tetratomic radicle $C^8H^{14}$, etc., correspond to the saturated hydrocarbide $C^8H^{18}$.

Experience has shown that 1 atom of oxygen may be substituted for 2 atoms of hydrogen in all monatomic radicles; that 1 atom of oxygen may be substituted for 2 atoms of hydrogen, or 2 atoms of oxygen for 4 atoms of hydrogen, in all biatomic radicles; that 1, 2, or 3 atoms of oxygen may be substituted for 2, 4, or 6 atoms of hydrogen in all triatomic radicles; in a word, that in any hydrocarbon whatever O may be substituted for $H^2$ any number of times equal to the number representing the atomicity of the radicle.

These substitutions do not alter the atomicity of the radicle at all, this remains as it was before. Only, the radicle becomes more and more electro-negative as the oxygen more completely replaces the hydrogen. The same saturated hydrocarbide may therefore give rise to a great number of radicles either oxygenated or not.

For instance, the following radicles would correspond to the hydrocarbide $C^8H^{18}$:

| | | | | | |
|---|---|---|---|---|---|
| $C^8H^{17\prime}$ | $C^8H^{16\prime\prime}$ | $C^8H^{15\prime\prime\prime}$ | $C^8H^{14\text{iv}}$ | $C^8H^{13\text{v}}$ | $C^8H^{12\text{vi}}$ |
| $C^8H^{15\prime}O$ | $C^8H^{14}O^{\prime\prime}$ | $C^8H^{13}O^{\prime\prime\prime}$ | $C^8H^{12}O^{\text{iv}}$ | $C^8H^{11}O^{\text{v}}$ | $C^8H^{10}O^{\text{vi}}$ |
| | $C^8H^{12}O^{2\prime\prime}$ | $C^8H^{11}O^{2\prime\prime\prime}$ | $C^8H^{10}O^{2\text{iv}}$ | $C^8H^9O^{2\text{v}}$ | $C^8H^8O^{2\text{vi}}$ |
| | | $C^8H^9O^{3\prime\prime\prime}$ | $C^8H^8O^{3\text{iv}}$ | $C^8H^7O^{3\text{v}}$ | $C^8H^6O^{3\text{vi}}$ |
| | | | $C^8H^6O^{4\text{iv}}$ | $C^8H^5O^{4\text{v}}$ | $C^8H^4O^{4\text{vi}}$ |
| | | | | $C^8H^3O^{5\text{v}}$ | $C^8H^2O^{5\text{vi}}$ |
| | | | | | $C^8O^{6\text{vi}}$ |

Each of these radicles may give rise to a number of compounds which will be grouped round it as a centre.

Such an assemblage of compounds has been called a group, and the radicle round which they are arranged is called the pivot of the group.

The different central or pivot radicles of groups naturally belong to the hydrocarbide from which they are derived, and which is called their fundamental hydrocarbide.

The aggregate of all the groups which collect round a fundamental hydrocarbide forms what is called a heterologous series.

Saturated hydrocarbides are not the only ones that are capable of forming heterologous series. Any non-saturated hydrocarbide whatever can, in certain conditions, act as if it were saturated, the only difference being in the properties of the compounds formed, which are always of the same degree of saturation as the hydrocarbide whence they are derived.

The result is that, to each term of the first homologous series, there should correspond, according to the principle of saturation, a single heterologous series, two to each term of the second, three to the third, and so on.

The aggregates of different heterologous series, the terms of which are isomeric, each with each, and which only differ in their degree of saturation, constitute series of a new order, which as yet have received no name, because no one but myself has indicated their possibility. They may be called eikologous series, from the Greek word εἰκώς, *similar*.

Thus around each radicle there ranges a *group* of which it is the pivot. The different groups united round the same fundamental hydrocarbide constitute a *heterologous* series. The different heterologous series derived from isomeric fundamental hydrocarbides form an *eikologous* series. The different eikologous series, all the terms of which are homologous among themselves, form a *homologous* series. Finally, the whole of the homologous series form the great isologous series which comprises all bodies in organic chemistry.

I say that the preceding series contain all the bodies in organic chemistry, though the place certain compounds ought to occupy is still unknown. This ignorance is not owing to the fact that these compounds have not their places in these series, but that they have as yet been too little studied for their places to be known.

All the bodies whose serial classification may be imagined are far from being known. Only three homologous series have been much studied: that in which hydrocarbides have the general formula $C^nH^{2n+2}$, that in which they have the formula $C^nH^{2n}$, and that in which their formula is $C^nH^{2n-6}$. In all the other series only a few terms here and there are known; the others remain to be discovered. Moreover, the classification allows us to foresee an immense number of isomers of which very few are as yet known, and which can only be discovered after new and numerous experiments.

We are far, however, from affirming that all the bodies indicated are really possible. In the deductions which have served to establish their formulæ, we have not taken into account the laws according to which the stability of bodies decreases as the molecule becomes complicated, which laws would greatly limit the number of compounds that can be realised. These laws are not known as yet, and will only be so when numerous discoveries shall have rendered the series more complete than they are at present. The actual classification is therefore only a large table which includes formulæ, deduced algebraically, of all organic compounds whether possible or not. The knowledge of the laws which regulate the stability of bodies will alone complete this classification by assigning to it its true limits.

It is evident that, starting from the atomicity of any body, the series of all its compounds which are theoretically possible may be algebraically deduced; and later, the series of its compounds that are really possible, when the laws governing the stability of bodies shall be known.

The elements being classed in series according to their atomicity on one side, and according to their electric polarity on the other, the whole of chemistry will constitute an immense series.

Finally, in all these series the physical and chemical properties being modified according to laws which may be discovered, we can foresee a state of chemistry in which, without studying the properties of different bodies in detail, and knowing only the number, atomicity, and electric polarity of the elements, it will be possible to determine by simple calculation the formulæ, properties, and mode of generation of all compounds possible We need not point out how important might be the results indicated in this conception.

## HYDROCARBIDES.

**Hydrocarbides corresponding to the Formula** $C^nH^{2n+2}$. — This series only contains, and can only contain, saturated hydrocarbides.

Natural State, Preparation. 1st.—Many hydrocarbides of this series are found native. The gas ($CH^4$) is disengaged in marshes, and Messrs. Cahours and Pelouze have extracted from the petroleums of America, by means of fractional distillation, the compounds

$$C^4H^{10},\ C^5H^{12},\ C^6H^{14},\ C^7H^{16},\ C^8H^{18},\ C^9H^{20},\ C^{10}H^{22},\ C^{11}H^{24},\ C^{12}H^{26},\ C^{13}H^{28},\ C^{14}H^{30},\ C^{15}H^{32},\ \text{and}\ C^{16}H^{34}.$$

Moreover, according to these chemists, it cannot be doubted that the parts of petroleum which boil at a higher temperature than the compound ($C^{16}H^{34}$) also contain other hydrocarbides which are homologues of the preceding ones.

2nd. These hydrocarbides are formed when acids answering either to the formula ($C^{n+1}H^{2n+2}O^2$) or to ($C^{n+2}H^{2n+2}O^4$) are submitted to influences which cause them to lose carbonic anhydride:

$$(C^{n+1}H^{2n+2}O^2) = \underset{\text{Carbonic anhydride.}}{(CO^2)} + (C^nH^{2n+2})$$

$$(C^{n+2}H^{2n+2}O^4) = \underset{\text{Carbonic anhydride.}}{2(CO^2)} + (C^nH^{2n+2})$$

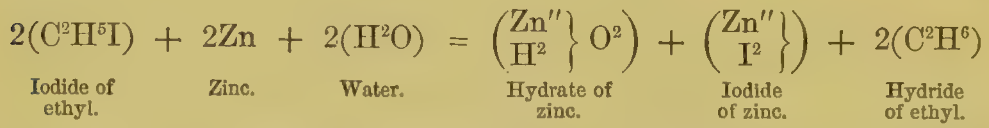
Generally, these acids are heated with an excess of alkali: it is, however, important to remark that at the temperature at which it is necessary to operate, the carbonic anhydride exercises an oxidizing action on the hydrocarbides formed. Instead of the saturated bodies of which we spoke, products are generally obtained less hydrogenized in consequence of this secondary reaction. Nevertheless, marsh gas can be readily prepared by this process by means of acetic acid, and the hydrides of hexyl and octyl by means of suberic and sebacic acid:

$$\underset{\text{Acetate of potassium.}}{(C^2H^3KO^2)} + \underset{\text{Potash.}}{(KHO)} = \underset{\text{Carbonate of potassium.}}{(CK^2O^3)} + \underset{\text{Marsh gas.}}{(CH^4)}$$

$$\underset{\text{Suberate of potassium.}}{(C^8H^{12}K^2O^4)} + \underset{\text{Potash.}}{2(KHO)} = \underset{\text{Carbonate of potassium.}}{2(CK^2O^3)} + \underset{\text{Hydride of hexyl.}}{(C^6H^{14})}$$

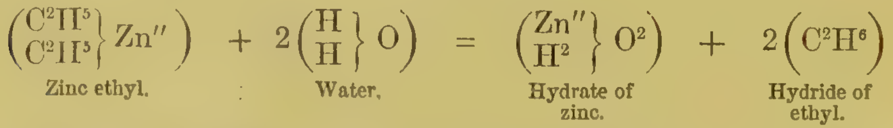
$$\underset{\text{Sebate of potassium.}}{(C^{10}H^{16}K^2O^4)} + \underset{\text{Potash.}}{2(KHO)} = \underset{\text{Carbonate of potassium.}}{2(CK^2O^3)} + \underset{\text{Hydride of octyl.}}{(C^8H^{18})}$$

3rd. The same hydrocarbides are obtained by submitting to the simultaneous action of zinc and water compounds derived from the corresponding alcohols, and which represent the hydrocarbide sought for, in which an atom of hydrogen is replaced by iodine. This operation ought to take place in hermetically-sealed tubes, and requires a temperature of about 200°.



$$\underset{\text{Iodide of ethyl.}}{2(C^2H^5I)} + \underset{\text{Zinc.}}{2Zn} + \underset{\text{Water.}}{2(H^2O)} = \underset{\text{Hydrate of zinc.}}{\left(\left.\begin{matrix}Zn''\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Iodide of zinc.}}{\left(\left.\begin{matrix}Zn''\\I^2\end{matrix}\right\}\right)} + \underset{\text{Hydride of ethyl.}}{2(C^2H^6)}$$

Instead of heating the iodides of the hydrocarbon radicles water and zinc together, a combination of these radicles with zinc (organometallic compounds) may be first prepared, and this combination decomposed by water.



$$\underset{\text{Zinc ethyl.}}{\left(\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}Zn''\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Hydrate of zinc.}}{\left(\left.\begin{matrix}Zn''\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Hydride of ethyl.}}{2\left(C^2H^6\right)}$$

4th. These hydrocarbons may also be prepared by means of others containing two atoms of hydrogen less than they, and many of which have been obtained by direct synthesis by means of their elements.

In order to obtain the carbides of hydrogen ($C^nH^{2n+2}$) by means of the carbides ($C^nH^{2n}$), these latter are combined with bromine. The compound formed ($C^nH^{2n}Br^2$) being heated to 275° with a mixture of iodide of potassium, copper, and water, decomposes. The hydrocarbide ($C^nH^{2n}$) is partly reconstituted and partly transformed into the hydrocarbide ($C^nH^{2n+2}$).

5th. One of these hydrocarbides, marsh gas ($CH^4$), has been obtained synthetically by the simultaneous action of sulphide of carbon and hydrosulphuric acid on copper heated to redness. In this case carbon and hydrogen are set free, and unite in the nascent state.

6th. Many of these hydrocarbides have been obtained by the action of red heat on butyrates and acetates.

7th. These bodies are formed during the dry distillation of boghead coal, cannel coal, and fatty substances.

8th. By distilling amylic alcohol with chloride of zinc, M. Wurtz has obtained the hydride of amyl ($C^5H^{12}$) and several of its homologues. Hydrocarbides belonging to the ($C^nH^{2n}$) series form at the same time in this reaction, as well as other hydrocarbides still less hydrogenized and as yet imperfectly studied.

9th. M. Schützenberger has recently discovered that the hydrocarbide ($C^2H^6$) (methyl or hydride of ethyl) is produced, mixed with carbonic anhydride, when hot acetic acid is made to act on the binoxide of barium.

$$\underset{\text{Acetic anhydride.}}{2\left(\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O\right)} + \underset{\text{Binoxide of barium.}}{\left(BaO^2\right)} = \underset{\text{Acetate of barium.}}{\left(Ba''\left\{\begin{matrix}OC^2H^3O\\OC^2H^3O\end{matrix}\right.\right)} + \underset{\text{Carbonic anhydride.}}{2\left(CO^2\right)} + \left(C^2H^6\right)$$

Properties.—1st. All these carbides of hydrogen are saturated, which signifies that none of them can unite either with chlorine, bromine, or monatomic radicles in general.

2nd. Submitted to the influence of bromine or chlorine, these hydrocarbides can exchange their hydrogen for these metalloids. Those of the compounds thus formed which contain a single atom of chlorine or bromine, are capable of exchanging this atom for the residue (OH), and an alcohol is then produced. When speaking of alcohols we shall see how this substitution is effected.

3rd. Trichlorinated products appear to decompose and form a monobasic acid answering to the formula ($C^nH^{2n}O^2$) under the influence of an alcoholic solution of potash. At least it has been proved that in these conditions trichlorinated marsh gas (chloroform) ($CHCl^3$) is transformed into formic acid, and trichlorinated hydride of ethyl into acetic acid.

$$\underset{\text{Trichlorinated hydrocarbide.}}{\left(C^nH^{2n-1}Cl^3\right)} + \underset{\text{Potash.}}{4\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Chloride of potassium.}}{3\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)} + \underset{\text{Potassic salt.}}{\left(C^nH^{2n-1}KO^2\right)}$$

$$+ \underset{\text{Water.}}{2\left(H^2O\right)}$$

4th. Nitric acid attacks the higher terms of this series, producing derivatives in which the hydrogen of the hydrocarbide is partially replaced by the group ($NO^2$). Thus, with the hydride of capryl ($C^8H^{18}$) the compound [$C^8H^{17}(NO^2)$] is obtained. The lower terms of the series do not undergo any alteration by nitric acid. But derivatives of these bodies in which the hydrogen is replaced by the radicle ($NO^2$) have been obtained indirectly. These compounds are called nitrous derivatives, and the substitution which gives rise to them is called nitrous substitution.

Starting from the hydrocarbide ($C^4H^{10}$) which can have two isomers, all the terms of this series may have some also, and the number of these isomers possible increases by one for each atom of carbon added to ($C^4H^{10}$). Thus ($C^5H^{12}$) might have three isomers, ($C^6H^{14}$) four, ($C^7H^{16}$) five, etc., all these isomers being equally saturated.

Nomenclature.—Several systems of nomenclature have been proposed for those hydrocarbides actually known: they were first supposed to be constituted by the union of a monatomic radicle with hydrogen, and they were called hydrides of these radicles.

Thus marsh gas ($CH^4$) has received the formula ($CH^3H$), and has been designated hydride of methyl; the gas ($C^2H^6$) has received the formula ($C^2H^5H$), and been named hydride of ethyl, etc.

Later, M. Berthelot proposed to take their names from the monobasic acids which are derived from them. Marsh gas has thus become *formene ;* hydride of ethyl, *acetene*, and so on.

Finally, Messrs. Cahours and Pelouze, applying to these bodies a nomenclature analogous to that Gerhardt adopted for the hydrocarburetted monatomic radicles derived from them, have proposed to deduce their names from the number of atoms of carbon they contain. Marsh gas thus becomes *protylene*, hydride of ethyl *deutylene*, etc.

We give below the formulæ of those of these hydrocarbides that are known, with the names corresponding to them in these three nomenclatures, the last of which seems to us the most preferable.

| | Gerhardt's names. | Berthelot's names. | Cahours and Pelouze's names. |
|---|---|---|---|
| $(CH^4)$ | Hydride of methyl | formene | protylene. |
| $(C^2H^6)$ | Hydride of ethyl | acetene | deutylene. |
| $(C^3H^8)$ | Hydride of propyl | propionene | tritylene. |
| $(C^4H^{10})$ | Hydride of butyl | butyrene | tetrylene. |
| $(C^5H^{12})$ | Hydride of amyl | valerene | pentylene. |
| $(C^6H^{14})$ | Hydride of hexyl | caproene | hexylene. |
| $(C^7H^{16})$ | Hydride of heptyl | œnanthylene | heptylene. |
| $(C^8H^{18})$ | Hydride of octyl | caprylene | octylene. |
| $(C^9H^{20})$ | Hydride of nonyl | pelargonene | nonylene. |
| $(C^{10}H^{22})$ | Hydride of decyl | | decylene. |
| $(C^{11}H^{24})$ | Hydride of undecyl | rutene | undecylene. |
| $(C^{12}H^{26})$ | Hydride of bidecyl | laurene | bidecylene. |
| $(C^{13}H^{28})$ | Hydride of tridecyl | cocinene | tridecylene. |
| $(C^{14}H^{30})$ | Hydride of tetradecyl | myrystene | tetradecylene. |
| $(C^{15}H^{32})$ | Hydride of pentadecyl | benene | pentadecylene. |
| $(C^{16}H^{34})$ | Hydride of hexadecyl | palmitene | hexadecylene. |

It must be remarked that the words hexylene, heptylene, octylene, nonylene—which are proposed by Messrs Cahours and Pelouze to designate the bodies $(C^6H^{14})$,$(C^7H^{16})$,$(C^8H^{18})$,$(C^9H^{20})$—are used by the greater number of chemists to designate the hydrocarbides :

$$(C^6H^{12}),(C^7H^{14}),(C^8H^{16}),(C^9H^{18}).$$

To avoid this confusion, though we consider the names used by Messrs. Cahours and Pelouze as excellent in themselves, we will use the names found in the first column.

### STUDY OF THE MOST IMPORTANT HYDROCARBIDES $(C^nH^{2n+2})$.

**Marsh Gas** $(CH^4)$.—This is produced naturally in marshes by the putrefaction of organic matters. On stirring stagnant waters, bubbles are seen to rise, which are a mixture of this gas, nitrogen, carbonic anhydride, and sometimes hydrosulphuric acid.

Marsh gas is found also unhappily in coal-mines, where it mixes with the air and forms an explosive gas known as fire-damp. The explosion takes places when the miners approach the inflammable gas with a lighted lamp. To avoid this accident, Davy surrounded the miner's lamp with a cylinder of fine wire gauze, which cools the flame, so that it is confined to the interior of the cylinder and cannot extend to the outside. As the internal explosion extinguishes these lamps, several platinum wires are fixed on the wick. These wires remain incandescent all the time the miner is in the inflammable atmosphere, and give sufficient light to direct his course. As Davy's lamp gives less light than the ordinary ones, owing to the cylinder of metallic gauze, tin reflectors are placed behind the flame. Fire-damp does not generally contain either olefiant gas ($C^2H^4$) or oxide of carbon.

Marsh gas also arises from the earth in many localities. Gas springs are known which have burned from time immemorial. Mud volcanoes, which are found in many places, are a species of muddy eruption caused by this gas.

Marsh gas is produced at the same time as other carbides of hydrogen when organic substances of a very simple constitution are heated to redness. M. Berthelot has obtained it by transmitting the vapours of formic acid ($CH^2O^2$) through a red-hot porcelain tube.

M. Dumas has made known a process by which this gas can be obtained in an almost pure state, and which consists in heating in a retort a mixture of two parts of crystallized acetate of sodium, two parts of hydrate of potassium, and three parts of powdered quicklime. The lime is to moderate the action of the potash on the glass of the retort, which it would otherwise break. The reaction is the following (*see* 2nd general process).

$$\underset{\text{Acetate of sodium.}}{(C^2H^3NaO^2)} + \underset{\text{Potash.}}{(KHO)} = \underset{\substack{\text{Carbonate of} \\ \text{potassium and sodium.}}}{(CNaKO^3)} + \underset{\text{Marsh gas.}}{(CH^4)}$$

M. Dumas' process is really an analytical one; but it has become synthetic since M. Kolbe has obtained the trichloracetic acid by means of its elements, and M. Melsens, acetic acid by means of trichloracetic acid.

M. Melsens has also succeeded in preparing marsh gas by submitting tetrachloride of carbon ($CCl^4$), which M. Kolbe obtains synthetically, to the action of nascent hydrogen, developed by means of water and the amalgam of sodium.

$$\underset{\substack{\text{Perchloride} \\ \text{of carbon.}}}{\left(CCl^4\right)} + \underset{\text{Hydrogen.}}{4\left(\begin{matrix}H \\ H\end{matrix}\right\}\Big)} = \underset{\substack{\text{Hydrochloric} \\ \text{acid.}}}{4\left(\begin{matrix}H \\ Cl\end{matrix}\right\}\Big)} + \underset{\text{Marsh gas.}}{\left(CH^4\right)}$$

M. Berthelot obtained this gas by transmitting a mixture of hydrosulphuric acid and vapour of sulphide of carbon over red-hot copper. The copper seizes the sulphur, while the carbon and hydrogen in a nascent state react on each other and combine. This reaction is very complicated: it gives rise not only to marsh gas, but to many other bodies.

Lastly, in order to obtain marsh gash perfectly pure, zinc-methyl must be decomposed by water (*see* 3rd general process.)

$$\underset{\text{Zinc-methyl.}}{\left(\left.\begin{matrix}CH^3\\CH^3\end{matrix}\right\}Zn''\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Hydrate of zinc.}}{\left(\left.\begin{matrix}Zn''\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Marsh gas.}}{2\left(CH^4\right)}$$

Marsh gas is colourless and has neither taste nor smell; it exercises no action on test paper, and requires 18·36 times its volume of water at 0° to dissolve it; its refracting power is 1·504 and its density 0·5576. It does not support respiration, but it is not poisonous. If mixed with a sufficient quantity of oxygen it may be breathed without danger. It burns readily with a dull flame. When mixed with air or oxygen it explodes on contact with an ignited body.

When this gas is passed through a red-hot tube, its volume is doubled, being converted into hydrogen at the same time as carbon is deposited. When decomposed by electricity the same result is produced.

$$\underset{\text{Marsh gas.}}{\left(CH^4\right)} = \underset{\text{Carbon.}}{C} + \underset{\text{Hydrogen.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}\right)}$$

In this reaction a small quantity of oily matter is also produced.

Chlorine acts very differently on marsh gas, according to the conditions of the experiment. If a mixture be made of four volumes of chlorine and two volumes of marsh gas, no reaction takes place in darkness, but under the influence of the electric spark or direct sunlight a violent explosion is the result; carbon is deposited and hydrochloric acid is formed: diffused light causes this reaction only after some time.

$$\underset{\text{Marsh gas.}}{\left(CH^4\right)} + \underset{\text{Chlorine.}}{2\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}\right)} = \underset{\text{Hydrochloric acid.}}{4\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Carbon.}}{C}$$

If, on the contrary, a mixture be made of one volume of marsh gas, one volume of carbonic anhydride and an excess of chlorine, a liquid is produced which contains chloroform and perchloride of carbon.

$$\underset{\text{Marsh gas.}}{\left(CH^4\right)} + \underset{\text{Chlorine.}}{3\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}\right)} = \underset{\text{Hydrochloric acid.}}{3\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Chloroform.}}{\left(CHCl^3\right)}$$

$$\underset{\text{Marsh gas.}}{\left(CH^4\right)} + \underset{\text{Chlorine.}}{4\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}\right)} = \underset{\text{Hydrochloric acid.}}{4\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Perchloride of carbon.}}{\left(CCl^4\right)}$$

If chlorine be made to react on an excess of marsh gas, either chloride of methyl or an isomer of this body is formed.

$$\underset{\text{Marsh gas.}}{\left(CH^4\right)} + \underset{\text{Chlorine.}}{\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}} = \underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Chloride of methyl.}}{\left(CH^3Cl\right)}$$

This latter body, submitted to the action of acetate of silver by M. Berthelot, has exchanged its chlorine for oxacetyl, and has thus furnished acetate of methyl from which methylic alcohol has been extracted by saponification.

$$\underset{\text{Chloride of methyl.}}{\left(CH^3Cl\right)} + \underset{\text{Acetate of silver.}}{\left(\left.\begin{matrix}C^2H^3O\\Ag\end{matrix}\right\}O\right)} = \underset{\text{Chloride of silver.}}{\left(AgCl\right)} + \underset{\text{Acetate of methyl.}}{\left(\left.\begin{matrix}CH^3\\C^2H^3O\end{matrix}\right\}O\right)}$$

$$\underset{\text{Acetate of methyl.}}{\left(\left.\begin{matrix}C^2H^3O\\CH^3\end{matrix}\right\}O\right)} + \underset{\text{Hydrate of potassium.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Acetate of potassium.}}{\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right)} + \underset{\text{Methylic alcohol.}}{\left(\left.\begin{matrix}CH^3\\H\end{matrix}\right\}O\right)}$$

Under the simultaneous influence of moisture, chlorine, and sunlight, marsh gas decomposes, giving hydrochloric acid and carbonic anhydride or oxide of carbon.

$$\underset{\text{Marsh gas.}}{\left(CH^4\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Chlorine.}}{4\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}\right)} = \underset{\text{Hydrochloric acid.}}{8\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Carbonic anhydride.}}{\left(CO^2\right)}$$

Bromine attacks this gas with difficulty.

Oxychloride of carbon converts it into hydrochloric acid and chloride of acetyl.

$$\underset{\text{Marsh gas.}}{(CH^4)} + \underset{\text{Chloride of carbonyl.}}{(CO''Cl^2)} = \underset{\text{Hydrochloric acid.}}{(HCl)} + \underset{\text{Chloride of acetyl.}}{\left(\begin{matrix}C\\ \\C\end{matrix}\left\{\begin{matrix}H^3\\ \overline{O}\\ Cl\end{matrix}\right.\right)}$$

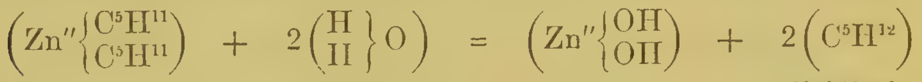
Concentrated nitric acid, even when mixed with sulphuric acid, has no action on marsh gas. It is the same with heated chloride of sulphur, perchloride of phosphorus and chloride of antimony.

**Hydride of Amyl** ($C^5H^{12}$).—Hydride of amyl is produced by the reaction of iodide of amyl on zinc and water (*see* 3rd general process) at a temperature of about 142°.

$$\underset{\text{Iodide of amyl.}}{2\left(C^5H^{11}I\right)} + \underset{\text{Zinc.}}{2\,Zn} + \underset{\text{Water.}}{2\left(H^2O\right)} = \underset{\text{Hydrate of zinc.}}{\left(\left.\begin{matrix}Zn''\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Iodide of zinc.}}{\left(Zn''I^2\right)}$$

$$+ \underset{\text{Hydride of amyl.}}{2\left(C^5H^{12}\right)}$$

Instead of causing water and zinc to act simultaneously on the iodide of amyl, zinc-amyl ($Zn''(C^5H^{11})^2$) may be decomposed by water.



$$\left(Zn''\begin{cases}C^5H^{11}\\C^5H^{11}\end{cases}\right) + 2\left(\begin{matrix}H\\H\end{matrix}\right\}O\Big) = \left(Zn''\begin{cases}OH\\OH\end{cases}\right) + 2\left(C^5H^{12}\right)$$

Zinc-amyl. Water. Hydrate of zinc. Hydride of amyl.

Hydride of amyl is also formed at the same time as amylene when amylic alcohol is decomposed by chloride of zinc. As the dehydration of amylic alcohol ought only to give amylene or homologues higher than this body, the production of the hydride of amyl is necessarily accompanied by that of hydrocarbides that are less hydrogenized than amylene (Wurtz). In order to obtain the hydride of amyl in a pure state, the product which passes between 30° and 40° is collected, treated with bromine, which seizes the amylene, and again distilled. The hydride of amyl, which boils at 30°, is then easily separated from the bromide of amylene, which boils at 90°.

Hydride of amyl is found ready formed in the petroleums of America.

It is a colourless and transparent liquid, very volatile, and has an agreeable ethereal odour; its density is 0·6385 at 14°·2, which makes it the lightest of all known liquids. It boils at 30°, and remains liquid at – 24°; its vapour density has been found to be 2·382.

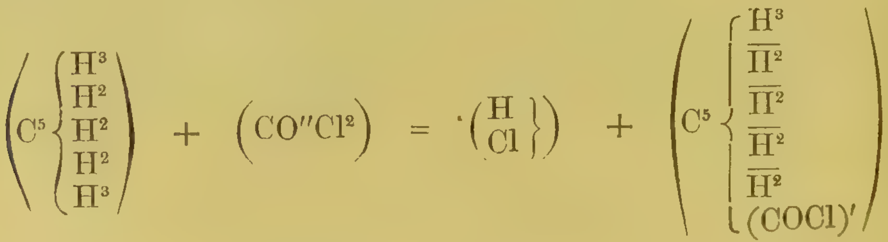
Hydride of amyl cannot be mixed with water, but it mixes in all proportions with alcohol and ether.

It burns with a very bright but sooty flame, but its vapour burns without smoke.

Concentrated sulphuric acid has no action on this body, neither has fuming nitric acid, nor a mixture of nitric and sulphuric acids.

When chlorine is substituted for the hydrogen of the hydride of amyl, the monochlorinated derivative appears to be identical with the chloride of amyl; at least it furnishes amylic alcohol when submitted to the action of acetate of silver, and the product of this reaction is saponified by alkalies.

The oxychloride of carbon, in acting on the vapour of hydride of amyl, gives rise to a double decomposition, the products of which are hydrochloric acid and chloride of caproyl.



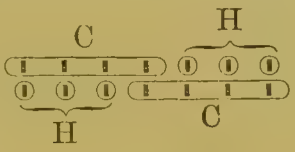
$$\left(C^5\begin{cases}H^3\\H^2\\H^2\\H^2\\H^3\end{cases}\right) + \left(CO''Cl^2\right) = \left(\begin{matrix}H\\Cl\end{matrix}\right\}\Big) + \left(C^5\begin{cases}H^3\\H^2\\H^2\\H^2\\H^2\\(COCl)'\end{cases}\right)$$

Hydride of amyl. Chloride of carbonyl. Hydrochloric acid. Chloride of caproyl.

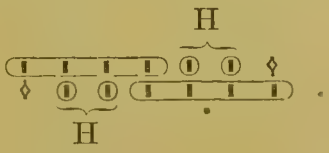
MEDICINE

**Hydrocarbides corresponding to the Formula ($C^nH^{2n}$).**—Theory leads us to expect two isomeric carburetted hydrogens for each term of this series, one saturated and the other acting as a biatomic radicle. When one of these hydrocarbides, either saturated or not, can have isomers of the same degree of saturation as itself, the number of these possible isomers is the same as the number of possible isomers of the hydrocarbide of the series ($C^nH^{2n+2}$) which contains the same quantity of carbon.

The constitution of the hydrocarbides that are actually known in this series is explained by admitting that it is the same as in the preceding series, with the slight difference that the chain they form is closed as shown in the following figure:

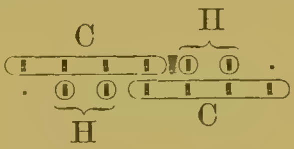


$C^nH^{2n+2}$



$C^nH^{2n}$

It might as easily be admitted that the chain is open, and that these hydrocarbides are not saturated, but it is impossible to decide this question. The following figure will show their constitution according to this latter hypothesis:



Preparation.—1st. These hydrocarbides may be prepared by the reaction of bodies which readily absorb moisture on alcohols differing from them by the elements of a molecule of water:

$$\underset{\text{Alcohol.}}{(C^2H^6O)} = \underset{\text{Water.}}{(H^2O)} + \underset{\text{Ethylene.}}{(C^2H^4)}$$

Concentrated sulphuric acid or chloride of zinc is generally used for this process. M. Wurtz has stated that when amylic alcohol ($C^5H^{12}O$) is treated with chloride of zinc, there is formed, besides amylene ($C^5H^{10}$) which corresponds to it, a great number of homologues higher in the series than this body. We have seen that hydride of amyl ($C^5H^{12}$) and its homologues are also obtained in this reaction at the same time as hydrocarbides which are less hydrogenized than those answering to the formula ($C^nH^{2n}$). These are not known in detail. It is singular that this phenomenon is not observed more with the caprylic alcohol ($C^8H^{18}O$), which, though more complicated than amylic alcohol, decomposes much more regularly than this latter, giving water and octylene ($C^8H^{16}$).

2nd. These hydrocarbides are also formed when acetates and butyrates are heated to redness. They are isolated from the products with which they are mixed by combining them with bromine, and are then separated from their bromides by heating these to 275° with copper, water, and iodide of potassium. M. Berthelot, to whom we owe the knowledge of this reaction, has thus obtained ethylene ($C^2H^4$), propylene ($C^3H^6$), butylene ($C^4H^8$), and amylene ($C^5H^{10}$).

3rd. These compounds are also formed by the action of a mixture of sulphide of carbon in vapour and sulphuretted hydrogen on red-hot copper.

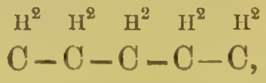
4th. One of these hydrocarbides, amylene, may be produced by causing zinc-ethyl to react on the iodide of allyl:

$$\underset{\text{Iodide of allyl.}}{2\left(\left.\begin{matrix}C^3H^5\\ I\end{matrix}\right\}\right)} + \underset{\text{Zinc-ethyl.}}{\left(\left.\begin{matrix}(C^2H^5)^2\\ Zn''\end{matrix}\right\}\right)} = \underset{\text{Iodide of zinc.}}{\left(\left.\begin{matrix}Zn''\\ I^2\end{matrix}\right\}\right)} + \underset{\text{Amylene.}}{2\left(C^5H^{10}\right)}$$

or the iodide of ethyl on the iodide of allyl in presence of sodium:

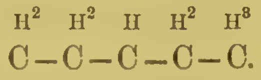
$$\underset{\text{Iodide of ethyl.}}{\left(\left.\begin{matrix}C^2H^5\\ I\end{matrix}\right\}\right)} + \underset{\text{Iodide of allyl.}}{\left(\left.\begin{matrix}C^3H^5\\ I\end{matrix}\right\}\right)} + \underset{\text{Sodium.}}{\left.\begin{matrix}Na\\ Na\end{matrix}\right\}} = \underset{\text{Iodide of sodium.}}{2\left(\left.\begin{matrix}Na\\ I\end{matrix}\right\}\right)} + \underset{\text{Amylene.}}{\left(C^5H^{10}\right)}$$

But amylene thus obtained is isomeric and not identical with ordinary amylene. While this latter answers to the formula



$$\overset{H^2}{C}-\overset{H^2}{C}-\overset{H^2}{C}-\overset{H^2}{C}-\overset{H^2}{C},$$

artificial amylene appears to correspond to the formula



$$\overset{H^2}{C}-\overset{H^2}{C}-\overset{H}{C}-\overset{H^2}{C}-\overset{H^3}{C}.$$

5th. By causing hydriodic acid to act on mannite, an iodized body (hydriodate of hexylene) answering to the formula ($C^6H^{12},HI$) has been obtained. This body, when treated with oxide of silver, furnishes hexylene:

$$\underset{\text{Hydriodate of hexylene.}}{2(C^6H^{12}HI)} + \underset{\text{Oxide of silver.}}{(Ag^2O)} = \underset{\text{Iodide of silver.}}{2(AgI)} + \underset{\text{Water.}}{(H^2O)} + \underset{\text{Hexylene.}}{2(C^6H^{12})}$$

Butylene ($C^4H^8$) has been procured by a similar process, using erythrite instead of mannite.

6th. These bodies are obtained by transmitting the hydrochloric ethers of corresponding alcohols over lime, heated to dull redness:

$$\underset{\text{Chloride of amyl.}}{2(C^5H^{11}Cl)} + \underset{\text{Lime.}}{(CaO)} = \underset{\text{Chloride of calcium.}}{(Ca''Cl^2)} + \underset{\text{Water.}}{(H^2O)} + \underset{\text{Amylene.}}{2(C^5H^{10})}$$

7th. M. Berthelot has obtained propylene ($C^3H^6$) by transmitting a mixture of marsh gas and oxide of carbon through a red-hot tube:

$$\underset{\text{Oxide of carbon.}}{(CO)} + \underset{\text{Marsh gas.}}{2(CH^4)} = \underset{\text{Propylene.}}{(C^3H^6)} + \underset{\text{Water.}}{(H^2O)}$$

8th. Propylene has also been prepared by Messrs. Alexeïeff and Beilstein by means of chloroform and zinc-ethyl:

$$\underset{\text{Chloroform.}}{2(CHCl^3)} + \underset{\text{Zinc-ethyl.}}{3(C^2H^5)^2Zn'')} = \underset{\text{Chloride of zinc.}}{3(ZnCl^2)} + \underset{\text{Propylene.}}{4(C^3H^6)} + \underset{\text{Marsh gas.}}{2(CH^4)}$$

9th. Compounds known as hydrates of tetrammoniums which result from the substitution of four atoms of an alcohol radicle for four atoms of hydrogen of the oxide of ammonium, separate by distillation into a ternary ammonia and an hydrocarbide ($C^nH^{2n}$):

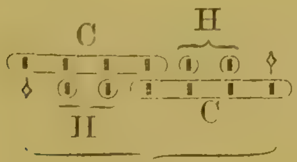
$$\underset{\text{Hydrate of tetrethyl-ammonium.}}{\left(\left.\begin{matrix}N(C^2H^5)^4\\ H\end{matrix}\right\} O\right)} = \underset{\text{Triethylamine.}}{\left(N(C^2H^5)^3\right)} + \underset{\text{Water.}}{\left(H^2O\right)} + \underset{\text{Ethylene.}}{\left(C^2H^4\right)}$$

When several different radicles are substituted for the hydrogen of the ammonium, the one containing the least carbon is eliminated in the state of carburetted hydrogen ($C^nH^{2n}$).

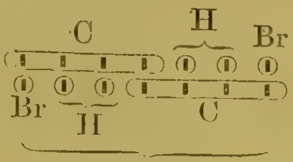
The hydrate of tetramethyl-ammonium, instead of giving methylene by distillation, furnishes methylic alcohol and trimethylamine; this is owing to the methylene being unable to exist in an isolated state:

$$\underset{\text{Hydrate of tetramethyl-ammonium.}}{\left(\left.\begin{matrix}N(CH^3)^4\\ H\end{matrix}\right\} O\right)} = \underset{\text{Trimethylamine.}}{\left(N(CH^3)^3\right)} + \underset{\text{Methylic alcohol.}}{\left(\left.\begin{matrix}CH^3\\ H\end{matrix}\right\} O\right)}$$

PROPERTIES.—1st. The hydrocarbides of this series act as biatomic radicles. They unite directly with chlorine, bromine, or iodine, giving compounds, which correspond to the formulæ ($C^nH^{2n}Cl^2$), ($C^nH^{2n}Br^2$), ($C^nH^{2n}I^2$). This reaction is explained by admitting that the hydrocarburetted compound, which first formed a closed chain, changes its constitution in presence of the halogen metalloids. These latter would open the chain.



Closed chain.



Open chain.

If, as we have seen it may be supposed, these hydrocarbides formed an open non-saturated chain, their union with chlorine or its congeners would consist in a simple addition.

The chlorinated, brominated, or iodized compounds, submitted to the action of an alcoholic solution of potash, lose one atom of hydrogen and one atom of their halogen metalloid, a haloid salt of potassium, and water being produced:

$$\underset{\substack{\text{Bromide of}\\\text{ethylene.}}}{\left(C^2H^4Br^2\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\substack{\text{Bromide of}\\\text{potassium.}}}{\left(\left.\begin{matrix}K\\Br\end{matrix}\right\}\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\substack{\text{Brominated}\\\text{ethylene.}}}{\left(C^2H^3Br\right)}$$

The chlorinated, brominated, or iodized hydrocarbide thus produced can in its turn fix $Cl^2$, $Br^2$, or $I^2$; then a molecule of hydrochloric, hydrobromic, or hydriodic acid can be taken from this new product by means of an alcoholic solution of potash. The body which is formed is still capable of fixing $Br^2$, $Cl^2$, or $I^2$; then of losing (HBr), (HCl) or (HI); and, by a succession of identical reactions, compounds are obtained which represent the original hydrocarbide, all the hydrogen of which is replaced by chlorine and its congeners, and the bichlorides, bibromides, and biniodides of these latter bodies.

Taking ethylene for example, the two following groups of brominated compounds may be derived from it:

| | | | |
|---|---|---|---|
| Ethylene . . . . | $C^2H^4$ | Bromide of ethylene . . . . | $C^2H^4Br$ |
| Brominated ethylene . | $C^2H^3Br$ | Bromide of brominated ethylene . | $C^2H^3Br,Br^2$ |
| Bibrominated ethylene . | $C^2H^2Br^2$ | Bromide of bibrominated ethylene | $C^2H^2Br^2,Br^2$ |
| Tribrominated ethylene | $C^2HBr^3$ | Bromide of tribrominated ethylene | $C^2HBr^3,Br^2$ |
| Perbrominated ethylene | $C^2Br^4$ | Bromide of perbrominated ethylene | $C^2Br^4,Br^2$ |

With the homologues of ethylene, two groups of analogous derivatives are obtained.

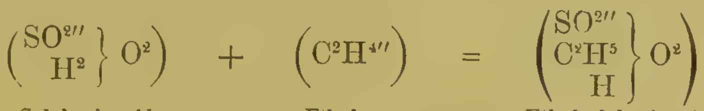
The monochlorinated or monobrominated hydrocarbide, instead of fixing $Cl^2$ or $Br^2$, may lose the atom of chlorine or bromine it contains in the state of hydrochloric or hydrobromic acid, and give rise to a carbide of hydrogen of another series. This reaction is produced at from 130° to 150° under the influence of alcoholic solution of potash, or, what is better, of ethylate of sodium:

$$\underset{\substack{\text{Brominated}\\\text{ethylene.}}}{\left(C^2H^3Br\right)} + \underset{\substack{\text{Ethylate of}\\\text{sodium.}}}{\left(\left.\begin{matrix}C^2H^5\\Na\end{matrix}\right\}O\right)} = \underset{\substack{\text{Bromide of}\\\text{sodium.}}}{\left(\left.\begin{matrix}Na\\Br\end{matrix}\right\}\right)} + \underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)} + \underset{\text{Acetylene.}}{\left(C^2H^2\right)}$$

Bromide of ethylene and its homologues, when treated by acetate of silver or acetate of potassium, lose their bromine and give rise to bodies which result from the replacement of each atom of bromine by the halogen residue of the acetates ($C^2H^3O^2$). We shall presently see (biatomic alcohols) how the formation of these products may be accounted for.

The bromides ($C^nH^{2n}Br^2$) when heated to 275° with a mixture of iodide of potassium, copper, and water, lose their bromine and re-form the carburetted hydrogen which was present in the bromide. A certain quantity of corresponding saturated carbide ($C^nH^{2n+2}$) is also produced in this reaction. Thus the bromide of ethylene ($C^2H^4Br^2$) in this case gives a mixture of ethylene ($C^2H^4$) and hydride of ethyl ($C^2H^6$).

2nd. The carburetted hydrogens ($C^nH^{2n}$) are capable of uniting with concentrated sulphuric acid after longer or shorter agitation together :



$$\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right) + (C^2H^{4''}) = \left(\left.\begin{matrix}SO^{2''}\\C^2H^5\\H\end{matrix}\right\}O^2\right)$$

Sulphuric acid. Ethylene. Ethylsulphuric acid.

The product distilled with water re-forms sulphuric acid, along with a body which is either an alcohol or the isomer of an alcohol.

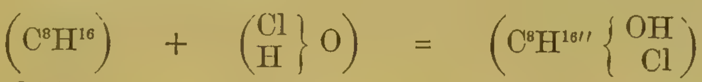
3rd. With Nordhausen acid they give sulpho-conjugate acids which are isomers of the preceding, but which boiling water does not decompose with formation of alcohol.

4th. Hydrochloric, hydrobromic, and hydriodic acids combine with these hydrocarbides. When submitted to the action of oxide of silver in presence of water, the compounds thus formed give rise to two simultaneous reactions. One portion of the body loses its halogen metalloid, which is replaced by the group (HO), forming an alcohol, or more generally a pseudo-alcohol; another portion loses hydrochloric, hydrobromic, or hydriodic acid, and reproduces the original hydrocarbide :

1st. $$\underset{\text{Hydriodate of ethylene.}}{2(C^2H^4HI)} + \underset{\text{Oxide of silver.}}{Ag^2O} + \underset{\text{Water.}}{H^2O} = \underset{\text{Iodide of silver.}}{2(AgI)} + \underset{\text{Ordinary alcohol.}}{2(C^2H^6O)}$$

2nd. $$\underset{\text{Hydriodate of hexylene.}}{2(C^6H^{12}HI)} + \underset{\text{Oxide of silver.}}{(Ag^2O)} = \underset{\text{Iodide of silver.}}{2(AgI)} + \underset{\text{Hexylene.}}{2(C^6H^{12})} + \underset{\text{Water.}}{(H^2O)}$$

5th. Hypochlorous acid combines directly with these hydrocarbides, and gives a monochlorhydrin of glycol, which corresponds to them :



$$(C^8H^{16}) + \left(\left.\begin{matrix}Cl\\H\end{matrix}\right\}O\right) = \left(C^8H^{16''}\left\{\begin{matrix}OH\\Cl\end{matrix}\right.\right)$$

Octylene. Hypochlorous acid. Octylenic chlorhydrin.

6th. Chloride of sulphur ($SCl^2$) unites directly with the hydrocarbides of the ($C^nH^{2n}$) series, giving rise to compounds which are both chlorinated and sulphuretted.

$$\underset{\text{Amylene.}}{(C^5H^{10})} + \underset{\text{Chloride of sulphur.}}{(Cl^2S)} = \underset{\text{New body.}}{(C^5H^{10}Cl^2S)}$$

NOMENCLATURE.—Those hydrocarbides of this series which are known are arranged in the following table :

| | |
|---|---|
| Ethylene . . . . . . . . . . . | $C^2H^4$ |
| Propylene . . . . . . . . . . . | $C^3H^6$ |
| Butylene . . . . . . . . . . . | $C^4H^8$ |
| Amylene . . . . . . . . . . . | $C^5H^{10}$ |
| Hexylene . . . . . . . . . . . | $C^6H^{12}$ |

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| | |
|---|---|
| Heptylene | $C^7H^{14}$ |
| Octylene | $C^8H^{16}$ |
| Nonylene | $C^9H^{18}$ |
| Decylene | $C^{10}H^{20}$ |
| Undecylene | $C^{11}H^{22}$ |
| ⋮ | ⋮ |
| Cetene | $C^{16}H^{32}$ |
| ⋮ | ⋮ |
| Cerotene (paraffin) | $C^{27}H^{54}$* |
| ⋮ | ⋮ |
| Melene | $C^{30}H^{60}$ |

### STUDY OF THE MOST IMPORTANT HYDROCARBIDES OF THE $C^nH^{2n}$ SERIES.

**Ethylene or Olefiant Gas** ($C^2H^4$).—This gas is produced at the same time as marsh gas and other bodies, when organic substances are submitted to dry distillation. It is also produced by transmitting hydrosulphuric acid and sulphide of carbon over red-hot copper.

This body has been obtained synthetically by causing nascent hydrogen, disengaged by the reciprocal action of zinc and ammonia at 40°, to act on cuprous acetylide.

$$\underset{\text{Oxide of cuprous acetyl.}}{\left.\begin{matrix}(C^2HCu^{2''})'\\(C^2HCu^{2''})'\end{matrix}\right\}O} + \underset{\text{Hydrogen.}}{4\left(\left.\begin{matrix}H\\H\end{matrix}\right\}\right)} = \underset{\text{Ethylene.}}{2(C^2H^4)} + \underset{\text{Copper.}}{4Cu} + \underset{\text{Water.}}{(H^2O)}$$

Ethylene may be prepared by the direct combination of carbon and hydrogen under the influence of a strong current of electricity; this is a direct synthesis.

The quickest and easiest way of preparing pure ethylene consists in gently heating alcohol with five or six times its weight of sulphuric acid or with chloride of zinc. The gas should be passed through lime-water to remove the acid vapours it might take with it, and through concentrated sulphuric acid to fix the vapours of alcohol and ether. As the mass swells out greatly, the operation must be conducted in a large flask, at the bottom of which it is advisable to place sand previously washed with sulphuric acid.

The final reaction is a dehydratation of the alcohol.

$$\underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)} = \underset{\text{Ethylene.}}{(C^2H^4)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

It is, however, probable that a compound at first forms which contains the elements of alcohol and sulphuric acid, and which is decomposed by heat producing the olefiant gas. When chloride of zinc is used, the salt appears to act simply as a dehydrant.

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* ($C^{27}H^{56}$) ?—TR.

A mixture of four parts of powdered boracic anhydride and one part of alcohol may be substituted for the preceding mixtures in the preparation of ethylene, but this process is less convenient than the former.

Olefiant gas is colourless and tasteless, and has an ethereal odour. Its density is 0·9784. It liquefies under the simultaneous action of strong pressure and a cold of −110° produced by a mixture of ether and solid carbonic anhydride; it has not been solidified. When liquid, ethylene is transparent, and does not boil at −110°. Olefiant gas cannot be respired; it is insoluble in water and very slightly soluble in alcohol and ether.

Nordhausen sulphuric acid absorbs ethylene after some time. Ordinary concentrated sulphuric acid also absorbs it when the reaction is assisted by constant agitation. In this latter case, ethyl-sulphuric acid is formed, which when distilled with water forms alcohol.

$$\text{1st.}\quad \underset{\text{Ethylene.}}{\left(C^2H^4\right)} + \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2\prime\prime}\\ H^2\end{matrix}\right\}O^2\right)} = \underset{\text{Ethyl-sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2\prime\prime}\\ C^2H^5\\ H\end{matrix}\right\}O^2\right)}$$

$$\text{2nd.}\quad \underset{\text{Ethyl-sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2\prime\prime}\\ C^2H^5\\ H\end{matrix}\right\}O^2\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)} = \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2\prime\prime}\\ H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\ H\end{matrix}\right\}O\right)}$$

This gas is inflammable and burns with a very bright flame. When mixed with oxygen or air it explodes either by the electric spark or the application of a light.

Chloride of sulphur ($SCl^2$) combines with olefiant gas and gives a compound which answers to the formula ($C^2H^4SCl^2$).

Olefiant gas also combines with hydracids, forming simple ethers of ordinary alcohol.

$$\underset{\text{Ethylene.}}{\left(C^2H^4\right)} + \underset{\text{Hydriodic acid.}}{\left(\left.\begin{matrix}H\\ I\end{matrix}\right\}\right)} = \underset{\text{Iodide of ethyl.}}{\left(\left.\begin{matrix}C^2H^5\\ I\end{matrix}\right\}\right)}$$

When treated by hypochlorous acid it gives monochlorhydrin of glycol.

$$\underset{\text{Ethylene.}}{\left(C^2H^{4\prime\prime}\right)} + \underset{\text{Hypochlorous acid.}}{\left(\left.\begin{matrix}Cl\\ H\end{matrix}\right\}O\right)} = \underset{\text{Chlorhydrin of glycol.}}{\left(C^2H^{4\prime\prime}\left\{\begin{matrix}OH\\ Cl\end{matrix}\right.\right)}$$

With chlorine, bromine, and iodine it gives the compounds ($C^2H^4Cl^2$), ($C^2H^4Br^2$), ($C^2H^4I^2$). Chloride of ethylene has been called Dutch liquid. We refer to what we have said of their general properties for the manner in which these different compounds act with the alkalies.

**Amylene** ($C^5H^{10}$).—The best method of preparing amylene consists in leaving a mixture of amylic alcohol and pounded chloride of zinc in a stoppered flask for several days. The salt partly dissolves, and when the mixture has the consistence of syrup it is distilled. The product should be submitted to fractional distillation, because it not only contains amylene and hydride of amyl, but also a great number of homologues higher than these bodies. Moreover, the amylene and the hydride of amyl cannot be completely separated by fractional distillation, these two bodies having boiling points which are too near each other.

In the process just described, the chloride of zinc may be replaced by sulphuric acid diluted with its own volume of water, but the results obtained are not so good.

In these two cases the final reaction consists in a dehydratation of amylic alcohol.

$$\underset{\text{Amylic alcohol.}}{\left(\left.\begin{matrix}C^5H^{11}\\ H\end{matrix}\right\} O\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\} O\right)} + \underset{\text{Amylene.}}{\left(C^5H^{10}\right)}$$

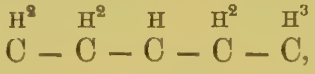
Amylene is also obtained by the reaction of the chloride of amyl with fused potash.

$$\underset{\text{Chloride of amyl.}}{(C^5H^{11}Cl)} + \underset{\text{Potash.}}{(KHO)} = \underset{\substack{\text{Chloride of}\\ \text{potassium.}}}{(KCl)} + \underset{\text{Water.}}{(H^2O)} + \underset{\text{Amylene.}}{(C^5H^{10})}$$

M. Wurtz has succeeded in preparing amylene synthetically by heating a mixture of iodide of ethyl and iodide of allyl with sodium.

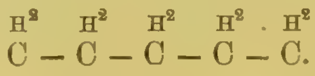
$$\underset{\substack{\text{Iodide of}\\ \text{ethyl.}}}{(C^2H^5I)} + \underset{\substack{\text{Iodide of}\\ \text{allyl.}}}{(C^3H^5I)} + \underset{\text{Sodium.}}{2\,Na} = \underset{\substack{\text{Iodide of}\\ \text{sodium.}}}{2\,(NaI)} + \underset{\text{Amylene.}}{(C^5H^{10})}$$

But, as we stated in the general description of the hydrocarbides of this series, artificial amylene has a constitution indicated by the formula



$$\overset{H^3}{C} - \overset{H^2}{C} - \overset{H}{C} - \overset{H^2}{C} - \overset{H^3}{C},$$

and is simply isomeric with the amylene obtained by means of amylic alcohol, the constitutional formula of which is



$$\overset{H^3}{C} - \overset{H^2}{C} - \overset{H^2}{C} - \overset{H^2}{C} - \overset{H^2}{C}.$$

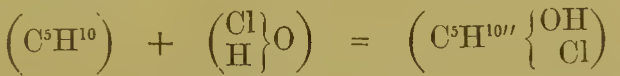
Amylene is a colourless, very mobile liquid, and has a very characteristic disagreeable smell; it boils at 35° according to Frankland, or at 39° according to Balard. Its flame is very luminous and sooty; its vapour density has been found to be 2·68 by Balard, to be 2·386 by Frankland, and 2·43 by Kékulé; its theoretical density being 2·4265.

Perchloride of antimony and sulphuric anhydride completely absorb the vapours of amylene.

Concentrated sulphuric acid dissolves amylene on agitation, but the hydrocarbide soon separates again in the form of a layer of oil, but its molecule is then doubled; it is no longer amylene, it is diamylene $(C^{10}H^{20})$.

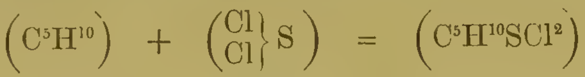
Hydracids heated with amylene combine with it directly. The compounds formed are not simple ethers of amylic alcohol but isomers of this body. When treated with moist oxide of silver, they furnish not amylic alcohol, but an isomer of this alcohol, the pseudo-amylic alcohol (*see* Pseudo-alcohols), mixed with the reconstituted amylene.

Hypochlorous acid combines with amylene and transforms it into amylenic chlorhydrin.



$$\underset{\text{Amylene.}}{\left(C^5H^{10}\right)} + \underset{\text{Hypochlorous acid.}}{\left(\left.\begin{matrix}Cl\\H\end{matrix}\right\}O\right)} = \underset{\text{Amylenic chlorhydrin.}}{\left(C^5H^{10\prime\prime}\left\{\begin{matrix}OH\\Cl\end{matrix}\right.\right)}$$

Chloride of sulphur $(SCl^2)$ also combines with amylene, forming a sulphuretted and chlorinated compound.



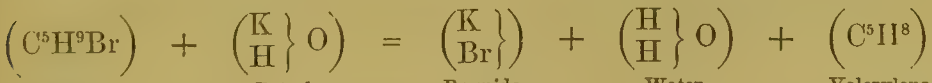
$$\underset{\text{Amylene.}}{\left(C^5H^{10}\right)} + \underset{\text{Chloride of sulphur.}}{\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}S\right)} = \underset{\text{New body.}}{\left(C^5H^{10}SCl^2\right)}$$

On treating amylene by halogen metalloids, and the products thus obtained, by alkalies; then by treating the bodies resulting from the action of the alkalies, as amylene was treated, a series of compounds will be formed, derived, some from amylene, and others from the chloride, bromide, or iodide of amylene by the substitution of the halogen metalloid for hydrogen.

Thus we know:

The bromide of amylene $(C^5H^{10}Br^2)$ and brominated amyleno $(C^5H^9Br)$; the bromide of brominated amylene $(C^5H^9BrBr^2)$ and bibrominated amylene $(C^5H^8Br^2)$.

When potash in alcoholic solution is heated in a sealed tube with brominated amylene, this loses $(HBr)$ and is transformed into valerylene (Reboul).



$$\underset{\text{Brominated amylene.}}{\left(C^5H^9Br\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Bromide of potassium.}}{\left(\left.\begin{matrix}K\\Br\end{matrix}\right\}\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Valerylene.}}{\left(C^5H^8\right)}$$

Treated by acetate of silver, the bromide of amylene exchanges $Br^2$ for $(C^2H^3O^2)^2$ and thus gives an acetate which, when saponified by alkalies, gives amyl-glycol. (*See* Glycols.)

**Hydrocarbides answering to the Formula $C^nH^{2n-2}$.**—Besides isomers of the same degree of saturation, theory indicates three isomers for each term, but up to the present time only one is known. The hydrocarbides which, while presenting the composition indicated, would be saturated or would act as only biatomic radicles, have not as yet been obtained. Those which act as tetratomic radicles are the only ones known.

Preparation.—There is only one general process by which these bodies are prepared; it consists in heating the monobrominated derivatives of hydrocarbides answering to the formula $C^nH^{2n}$ with the ethylate of sodium at a temperature of 130° to 150°.

$$\left(C^nH^{2n-1}Br\right) + \underset{\text{Ethylate of sodium.}}{\left(\left.\begin{matrix}C^2H^5\\ Na\end{matrix}\right\} O\right)} = \underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\ H\end{matrix}\right\} O\right)} + \underset{\text{Bromide of sodium.}}{\left(\left.\begin{matrix}Na\\ Br\end{matrix}\right\}\right)} + \left(C^nH^{2n-2}\right)$$

When these hydrocarbides are liquid they are separated from the excess of alcohol by washing them with water in which they are insoluble and the purification is completed by distillation.

When gaseous they are transmitted into an ammoniacal solution of protochloride of copper; a precipitate then forms which contains copper, and is very explosive. This precipitate, carefully washed and treated with hydrochloric acid, furnishes the gas in a pure state.

Those of these hydrocarbides which are liquid do not give rise to any reaction in presence of ammoniacal protochloride of copper.

Properties.—1st. When shaken with concentrated sulphuric acid these bodies are absorbed. On distilling the liquid with water, a product is obtained which represents the original hydrocarbide with a molecule of water added. This product is an alcohol or an isomer of an alcohol. This action of sulphuric acid has only been well studied with acetylene.

2nd. Treated by hydrobromic and hydriodic acids, and probably also by hydrochloric acid, these hydrocarbides absorb one or two molecules of these bodies. The bihydrobromates and bihydriodates produced have the same composition as the bibromides derived from the hydrocarbides corresponding to the series $C^nH^{2n}$, as the following equation shows:

$$(C^nH^{2n-2}, 2HBr) \quad = \quad (C^nH^{2n}Br^2).$$

But these two classes of bodies are isomeric, not identical.

Bromides of the hydrocarbides $C^nH^{2n}$ being capable of transformation into biatomic alcohols, it is probable that the bihydrobromates of which we speak can furnish isomers of these alcohols. This is almost certain, considering that M. Wurtz has obtained a similar result with the hydrocarbide ($C^6H^{10}$), diallyl, which, if it is not identical with, at least very nearly approaches by its properties to those of which we are here speaking.

3rd. These hydrocarbides combine either with one or two molecules of bromine, giving the compounds ($C^nH^{2n-2}Br^2$) and ($C^nH^{2n-2}Br^4$), the second of which is often crystallized. While studying bromides of this order prepared by means of valerylene ($C^5H^8$), M. Reboul observed that under the influence of potash in alcoholic solution the derivative ($C^5H^8Br^2$) loses first a molecule of hydrobromic acid, giving the bromides ($C^5H^7Br$); then a second molecule of this acid, and is transformed into a new hydrocarbide, to which he gives the name of valylene, and which answers to the formula ($C^5H^6$).

4th. Those hydrocarbides of this series which are gaseous, give an explosive precipitate in presence either of nitrate of silver or of ammoniacal chloride of copper. These precipitates vary in their constitution according to the gas from which they arise.

With acetylene, they answer to the formula $\left(\left.\begin{matrix}C^2HAg^2\\C^2HAg^2\end{matrix}\right\}O\right)$ or $\left(\left.\begin{matrix}(C^2HCu^{2''})'\\(C^2HCu^{2''})'\end{matrix}\right\}O\right)$, which makes them oxides of the organo-metallic radicles derived from vinyl ($C^2H^3$) by the substitution of biatomic $Ag^2$ or $Cu^2$ for $H^2$. M. Berthelot has given the names of argent-acetyl and cupros-acetyl to these radicles.

With allylene, the cupric precipitate appears to have a similar formula. But the argentic precipitate answers to the formula ($C^3H^3Ag$), which makes it a simple argentic derivative of allylene.

$$1\text{st.}\ \underset{\text{Oxide of argent-acetyl.}}{\left(\left.\begin{matrix}C^2HAg^2\\C^2HAg^2\end{matrix}\right\}O\right)} + 4\underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + 4\underset{\text{Chloride of silver.}}{\left(\left.\begin{matrix}Ag\\Cl\end{matrix}\right\}\right)} + 2\underset{\text{Acetylene.}}{\left(C^2H^2\right)}$$

$$2\text{nd.}\ \underset{\text{Argentic allylene.}}{(C^3H^3Ag)} + \underset{\text{Hydrochloric acid.}}{(HCl)} = \underset{\text{Chloride of silver.}}{(AgCl)} + \underset{\text{Allylene.}}{(C^3H^4)}$$

The oxides of argent-acetyl and cupros-acetyl are true basic oxides, whence a whole series of saline compounds is derived.

Nomenclature.—At present only four of these hydrocarbides are certainly known; these are:

| | | |
|---|---|---|
| Acetylene . . . . . . . | $C^2H^2$ | (Berthelot). |
| Allylene . . . . . . . | $C^3H^4$ | (Sawitsch). |
| Crotonylene . . . . . . | $C^4H^6$ | (Caventou). |
| Valerylene . . . . . . . | $C^5H^8$ | (Reboul). |

A hydrocarbide ($C^6H^{10}$) recently obtained by M. Caventou must be added to these. This hydrocarbide is not, as might be thought, identical, but simply isomeric with diallyl $\left(\left.\begin{matrix}C^3H^5\\C^3H^5\end{matrix}\right\}\right)$. The differences which exist between these bodies chiefly affect their physical properties. Their chemical properties are the same: thus diallyl unites directly with one or two molecules of bromine or hydriodic acid, like acetylene and its homologues.*

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* The following facts, recently discovered by M. Berthelot, must be added to what has been said of the hydrocarbides $C^nH^{2n}$ and $C^nH^{2n-2}$.

1st. When an aqueous solution of permanganate of potassium is gradually added to acetylene ($C^2H^2$) at the ordinary temperature, care being taken to shake it all the time, binoxide of manganese is deposited; the liquid, separated by filtering from this precipitate, contains a large quantity of oxalate of potassium, from which the oxalic acid can be extracted. This acid results from a direct oxidation.

$$\underset{\text{Acetylene.}}{(C^2H^2)} + \underset{\text{Oxygen.}}{4O} = \underset{\text{Oxalic acid.}}{(C^2H^2O^4)}$$

[At

**Hydrocarbides Corresponding to the Formula** $C^nH^{2n-4}$. — Independently of isomers of the same degree of saturation, four isomers ought to be found corresponding to each term of this series; one of these being saturated, a second biatomic, a third tetratomic, and a fourth hexatomic. In reality, we know the essence of turpentine and its isomers, which form tetratomic radicles, and among which perhaps biatomic radicles may also be found. Moreover, valylene ($C^5H^6$), recently discovered by M. Reboul, and which we mentioned when speaking of the hydrocarbides of the preceding series, is hexatomic.

In this series, the essence of turpentine and its isomers alone being well known, we will only speak of them.

ESSENCE OF TURPENTINE.—A hydrocarbide, the formula of which is ($C^{10}H^{16}$), is extracted from the *Pinus maritima*, and from the *Pinus australis* of the southern states of America. The hydrocarbides from

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At the same time formic acid and carbonic anhydride are formed, and these may be regarded as produced by the transformation of oxalic acid in the nascent state:

$$\begin{array}{ccccc} (C^2H^2O^4) & = & (CH^2O^2) & + & (CO^2) \\ \text{Oxalic acid.} & & \text{Formic acid.} & & \text{Carbonic anhydride.} \end{array}$$

Allylene ($C^3H^4$), a homologue of acetylene, also possesses the property of giving rise to a corresponding acid, malonic acid, by simply fixing oxygen, under the influence of permanganate of potassium, in the cold:

$$\begin{array}{ccccc} (C^3H^4) & + & 4O & = & (C^3H^4O^4) \\ \text{Allylene.} & & \text{Oxygen.} & & \text{Malonic acid.} \end{array}$$

This fixing of oxygen causes at the same time the formation of acetic acid and carbonic anhydride, that is to say, products of the decomposition of malonic acid:

$$\begin{array}{ccccc} (C^3H^4O^4) & = & (C^2H^4O^2) & + & (CO^2) \\ \text{Malonic acid.} & & \text{Acetic acid.} & & \text{Carbonic anhydride.} \end{array}$$

These latter reactions are, however, less clear than the preceding ones. In fact, it is always observed that oxalic acid and its products of decomposition, formic acid and carbonic anhydride, are also formed. It is probable that the oxalic acid results from the oxidation of acetic acid in the nascent state:

$$\begin{array}{ccccccc} (C^2H^4O^2) & + & 3O & = & (H^2O) & + & (C^2H^2O^4) \\ \text{Acetic acid.} & & \text{Oxygen.} & & \text{Water.} & & \text{Oxalic acid.} \end{array}$$

2nd. The oxidation of ethylene ($C^2H^4$), under the influence of permanganate of potassium, is almost as easy as that of acetylene. M. Berthelot has seen that, independently of the formic acid and carbonic anhydride discovered by M. Truchot in the products of this oxidation, there is produced oxalic acid, the formation of which represents the fundamental reaction:

$$\begin{array}{ccccccc} (C^2H^4) & + & 5O & = & (H^2O) & + & (C^2H^2O^4) \\ \text{Ethylene.} & & \text{Oxygen.} & & \text{Water.} & & \text{Oxalic acid.} \end{array}$$

Propylene also gives an analogous reaction to that of allylene:

$$\begin{array}{ccccccc} (C^3H^6) & + & 5O & = & (H^2O) & + & (C^3H^4O^4) \\ \text{Propylene.} & & \text{Oxygen.} & & \text{Water.} & & \text{Malonic acid.} \end{array}$$

Malonic acid is accompanied by secondary products, such as oxalic, formic, and acetic acids, and carbonic anhydride.

Amylene also appears to undergo the same oxidation under the influence of the permanganate of potassium, and is transformed into water and pyrotartaric acid.

these two sources are not identical; the former, known as French turpentine, is levogyrate, while that from America, called English turpentine, is dextrogyrate. These essences only differ in this particular property.

A great number of vegetables contain essences that are isomers or polymers of essence of turpentine: those which have the formula $C^{10}H^{16}$ are so easily confounded with essence of turpentine by their chemical properties, and those answering to a multiple formula have so many relations with the polymers that are obtained by modifying this latter, that the study of this body is the study of all these hydrocarbides, which scarcely differ except by their physical characters.

PROPERTIES.—1st. Essence of turpentine, when exposed to the air, absorbs oxygen which acquires the properties of ozone; then this oxygen enters into combination with the essence, and resinous products are formed. The action of strong oxidizing agents transforms this hydrocarbide into certain acids which are only slightly known.

2nd. When essence of turpentine is submitted to the action of a temperature of from 200° to 250°, it undergoes a transformation. Afterwards, on distillation, two bodies may be separated from it; one boils at 176° to 178°, and is levogyrate; it is called isoterebenthene or austrapyrolene: the other is volatile above 360°, and is also levogyrate; it is known as metaterebenthene or dipyrolene. The formula of the first of these hydrocarbides is $(C^{10}H^{16})$, like the essence from which it is derived; that of the second is $(C^{20}H^{32})$.

3rd. Treated by fluoride of boron or by concentrated sulphuric acid, essence of turpentine is transformed into two inactive hydrocarbides; one, volatile at 160° like the essence whence it is derived has its formula $(C^{10}H^{16})$, and has received the name of terebene; the other, volatile at a very high temperature, answers to the formula $(C^{20}H^{32})$, and is known as colophene or diterebene.

4th. On causing stearate of sodium to act at 200° on a solid compound of hydrochloric acid and essence of turpentine, which we shall presently study under the name of monohydrochlorate of turpentine, the carbide which has for formula $(C^{10}H^{16})$ is re-formed. This body has received the name of camphene; it is crystallized, and is levogyrate or dextrogyrate according as it is derived from French or English turpentine. On substituting acetate for stearate of sodium in its preparation, the same hydrocarbide is obtained, but it is then inactive.

Camphene, when submitted to the catalytic action of platinum black, appears to oxidize; in this case it is probable that laurel camphor may be formed:

$$\underset{\text{Camphene.}}{2\left(C^{10}H^{16}\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix} O \\ O \end{matrix}\right\}} = \underset{\text{Laurel camphor.}}{2\left(C^{10}H^{16}O\right)}$$

5th. Hydrochloric acid is capable of combining with the essence of turpentine in several proportions. When a gaseous current of hydrochloric acid is made to act on it, a product is obtained which has for formula $(C^{10}H^{16}HCl)$: it is the monochlorhydrate of turpentine: if, on the contrary, a concentrated aqueous solution of hydrochloric acid be made to act on the essence, and the action be continued for several weeks, crystals are deposited which have for formula $(C^{10}H^{16},2HCl)$, and which are called dichlorhydrate of terpilene. This dichlorhydrate may be obtained by means of the gaseous acid, by substituting the essence of lemon for its isomer the essence of turpentine; for this reason it is called dichlorhydrate of citrene.

On causing hydrochloric acid to act on terebene, a body is obtained which answers to the formula $[(C^{10}H^{16})^2,HCl] = (C^{20}H^{32},HCl)$; it is the subchlorhydrate of essence of turpentine or hydrochlorate of diterebene.

When a current of hydrochloric acid is directed through a solution of essence of turpentine in acetic acid, a hydrochlorate is obtained which is called intermediate hydrochlorate or hydrochlorate of dipyrolene: this body has the formula $(C^{20}H^{32},3HCl)$.

6th. Hydrobromic and hydriodic acids give rise to the same derivatives as hydrochloric acid, but the biniodhydrate is obtained by a different process (*see* 11th).

7th. When preparing mono- and dichlorhydrates, mono- and dibromhydrates, and the mon-iodhydrate of essence of turpentine, two isomers of each of these bodies are always obtained, one liquid, and the other solid and crystallized. The crystallized monochlorhydrate has been improperly called artificial camphor, and the crystallized dichlorhydrate, camphor of lemon.

8th. When a mixture of alcohol, nitric acid, and essence of turpentine is left for several months exposed to the air, a crystallized hydrate is deposited which has the formula $(C^{10}H^{16},2H^2O,+\text{aq.})$, and which is called terpine. Under the influence of heat, terpine loses its water of crystallization. The mother-liquors, from which terpine is deposited, contain a liquid isomer of this body.

9th. When the preceding mixture is left for several months in a hermetically-sealed vessel, care being taken that it is frequently shaken during this time, a liquid monochlorhydrate, answering to the formula $(C^{10}H^{16},H^2O)$, is produced.

10th. Terpine, under the influence of a small proportion of sulphuric acid, is transformed into another hydrate which has received the name of terpinol, the formula of which is $(C^{20}H^{32},H^2O)$. This compound is however obtained more readily by causing an alcoholic solution of potash to react on the dichlorhydrate of citrene, or acetate of silver on the dibromhydrate: the reaction in this latter case appears to be expressed by the following equation:

$$\underset{\text{Dibromhydrate of citrene.}}{2(C^{10}H^{18}Br^2)} + \underset{\text{Acetate of silver.}}{4(C^2H^3AgO^2)} = \underset{\text{Bromide of silver.}}{4(AgBr)} + \underset{\text{Acetic acid.}}{2(C^2H^4O^2)}$$

$$+ \underset{\text{Acetic anhydride.}}{\left(\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O\right)} + \underset{\text{Terpinol.}}{\left(C^{20}H^{34}O\right)} \qquad (\text{Oppenheim.})$$

11th. Terpine, when submitted to the action of the chloride, bromide, or iodide of phosphorus, gives rise to the dichlorhydrate dibromhydrate, or biniodhydrate of citrene. The latter body has only been obtained in this manner.

12th. Terpine, when heated with acetic anhydride, can, when the temperature is carefully regulated, give rise to a double decomposition, in consequence of which one of its atoms of hydrogen is replaced by the radicle acetyl ($C^2H^3O$). The body thus produced is allied to those which we shall study presently under the name of compound ethers in the chapter devoted to alcohols; it shows the alcoholic nature of terpine. Its formula is ($C^{10}H^{19}(C^2H^3O)O^2$), and is formed according to the equation:

$$\underset{\text{Terpine.}}{\left(C^{10}H^{20}O^2\right)} + \underset{\text{Acetic anhydride.}}{\left(\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O\right)} = \underset{\text{Acetic acid.}}{\left(\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O\right)} + \underset{\text{Monacetic terpine.}}{\left(C^{10}H^{19}(C^2H^3O)O^2\right)}$$

EPITOME OF THE THEORY OF THE DERIVATIVES OF THE ESSENCE OF TURPENTINE.—The hydrocarbide ($C^{10}H^{16}$) is tetratomic, and can therefore unite with four monatomic atoms, that is to say, with two molecules of hydrochloric, hydrobromic, or hydriodic acids; thence the dichlorhydrate, the dibromhydrate, and the biniodhydrate: but it can also unite with only a single molecule of these acids, that is to say, with two monatomic atoms; thence the monochlorhydrate, monobromhydrate, and mon-iodhydrate.

On being doubled, the tetratomic radicle ($C^{10}H^{16}$), like all polyatomic radicles, loses one part of its capacity for saturation, and the hydrocarbide ($C^{20}H^{32}$), which is hexatomic, is formed. This hydrocarbide is the radicle of the intermediate hydrochlorate and hydrobromate ($C^{20}H^{32}$,3HCl). . . .

As an hexatomic hydrocarbide ($C^{20}H^{32}$) ought to be able to produce non-saturated compounds with four or two monatomic atoms. The compounds with four monatomic radicles are still unknown. Those which contain only two of these radicles are known; they are the subchlorhydrate, the subbromhydrate, and the subiodhydrate ($C^{20}H^{32}$,HCl) . . . .

If in the different hydrochlorates each atom of chlorine be replaced by the residue HO, we shall have the formulæ of the different hydrates we have mentioned; the formula of an unknown hydrate, which would correspond to the intermediate hydrochlorate, will also be obtained.

In the following table we give the different derivatives of essence of turpentine, according to the preceding theory. The bodies which exist in solid and liquid modifications have been indicated by the Greek letters $\alpha$ and $\beta$, which are placed after their formulæ.

| **HYDROCARBIDES** $(C^{10}H^{16})^{IV}$, $\alpha\beta$ | | **HYDROCARBIDES** $(C^{20}H^{32})^{VI}$ | |
|---|---|---|---|
| Non-saturated Compounds. | Saturated Compounds. | Non-saturated Compounds. | Saturated Compounds. |
| $(C^{10}H^{17}Cl)$, $\alpha\beta$<br>Monochlorhydrate. | $(C^{10}H^{18}Cl^2)$, $\alpha\beta$<br>Dichlorhydrate. | $(C^{20}H^{33}Cl)$<br>Subchlorhydrate. | $(C^{20}H^{35}Cl)$<br>Intermediate chlorhydrate. |
| $(C^{10}H^{17}Br)$, $\alpha\beta$<br>Monobromhydrate. | $(C^{10}H^{18}Br^2)$, $\alpha\beta$<br>Dibromhydrate. | $(C^{20}H^{33}Br)$<br>Subbromhydrate. | $(C^{20}H^{35}Br^3)$<br>Intermediate bromhydrate. |
| $(C^{10}H^{17}I)$, $\alpha\beta$<br>Moniodhydrate. | $(C^{10}H^{18}I^2)$<br>Di-iodhydrate. | $(C^{20}H^{33}I)$<br>Subiodhydrate. | $(C^{20}H^{38}O^3)$<br>Intermediate hydrate (unknown). |
| $(C^{10}H^{18}O)$<br>Monohydrate. | $(C^{10}H^{20}O^2)$, $\alpha\beta$<br>Dihydrate (terpine). | $(C^{20}H^{34}O)$<br>Terpinol. | |
| | $(C^{10}H^{19}(C^2H^3O)O^2)$<br>Monacetic terpine. | | |

ESSENCES ISOMERIC WITH ESSENCE OF TURPENTINE.—The essences of athamanta, bergamotte, borneo, camphor, birch, camomile, caoutchouc, caraway, lemon, coriander, elemi, gaultheria, juniper, cloves, gamboge, hops, laurel, orange, parsley, pepper, savine, Tolu, thyme, valerian, and others, like essence of turpentine, have the formula $(C^{10}H^{16})$.*

The essences of cubebs and copaiba appear to have their formula a multiple of this, probably $(C^{20}H^{32})$.

**Hydrocarbides which have the Formula** $C^nH^{2n-6}$.—In this series, and without speaking of isomers of the same atomicity, theory leads us to anticipate for each term the existence of five isomeric hydrocarbides differing in their atomicity, which may vary from 0 to 8. The homologous series comprising all the bodies which are classed among these hydrocarbides has received the name of the aromatic series, because it comprises bodies which have an agreeable odour, like essence of bitter almonds, benzoic acid, essence of cumin, etc.

PREPARATION.—The hydrocarbides of this series are prepared by causing lime to act at red heat on monatomic acids, from which they differ by $(CO^2)$, or on biatomic acids from which they differ by $(C^2O^4)$.

| | | | | | | |
|---|---|---|---|---|---|---|
| $(C^7H^6O^2)$ | $+$ | $(CaO)$ | $=$ | $(CaCO^3)$ | $+$ | $(C^6H^6)$ |
| Benzoic acid. | | Lime. | | Carbonate of calcium. | | Benzine. |

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* We have seen that essence of turpentine may be transformed into several isomers, one of which, camphene $(C^{10}H^{16})$ is crystallized, and is capable of giving, with hydrochloric acid, the monochlorhydrate $(C^{10}H^{16},HCl)$, and never the dichlorate $(C^{10}H^{16},2HCl)$. This camphene is obtained by means of the monochlorhydrate decomposed by soap. MM. Lauth and Oppenheim have shown that aniline also decomposes the monochlorhydrate, producing camphene. The same chemists have likewise discovered that aniline also decomposes the dichlorhydrate. There is then produced a liquid isomeric with essence of turpentine, terpilene $(C^{10}H^{16})$, which, under the influence of hydrochloric acid, always gives the dichlorhydrate, and never the monochlorhydrate. M. Berthelot had obtained terpilene by the action of sodium on the dichlorhydrate of turpentine. But the method discovered by MM. Lauth and Oppenheim is more convenient, and gives better results.

$$\underset{\text{Phtalic acid.}}{(\mathrm{C^8H^6O^4})} + \underset{\text{Lime.}}{2(\mathrm{CaO})} = \underset{\text{Carbonate of calcium.}}{2(\mathrm{CaCO^3})} + \underset{\text{Benzine.}}{(\mathrm{C^6H^6})}$$

This mode of preparation is the same as one we gave for the preparation of marsh gas and its homologues.

2nd. These hydrocarbides can be prepared by submitting the corresponding alcohols to the action of an alcoholic solution of potash. This process has only been tried for toluene and cymene.

$$\underset{\text{Benzylic alcohol.}}{3\left(\mathrm{C^7H^8O}\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}\mathrm{K}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\text{Benzoate of potassium.}}{\left(\mathrm{C^7H^5KO^2}\right)} + \underset{\text{Toluene.}}{2\left(\mathrm{C^7H^8}\right)} + \underset{\text{Water.}}{2\left(\mathrm{H^2O}\right)}$$

3rd. A hydrocarbide of this series has been obtained by the dehydration of camphor by means of chloride of zinc or phosphoric anhydride:

$$\underset{\text{Laurel camphor.}}{(\mathrm{C^{10}H^{16}O})} = \underset{\text{Water.}}{(\mathrm{H^2O})} + \underset{\text{Cymene (cymol).}}{(\mathrm{C^{10}H^{14}})}$$

The same hydrocarbide, or at least an isomer, is found in a natural product, the essence of cumin.

4th. These different hydrocarbides exist in the oils which arise from the distillation of pit-coal, as well as in that which is separated from wood-spirit on treating the crude product with water.

5th. According to M. Riche, benzine is obtained by submitting chloride of phenyl to the action of sodium:

$$\underset{\text{Chloride of phenyl.}}{2\left(\mathrm{C^6H^5Cl}\right)} + \underset{\text{Sodium.}}{\left.\begin{matrix}\mathrm{Na}\\\mathrm{Na}\end{matrix}\right\}} = \underset{\text{Chloride of sodium.}}{2\left(\left.\begin{matrix}\mathrm{Na}\\\mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\text{Benzine.}}{\left(\mathrm{C^6H^6}\right)} + \underset{\text{Phenylene.}}{\left(\mathrm{C^6H^4}\right)}$$

It is probable that the homologues of chloride of phenyl, if treated by sodium, would furnish the homologues of benzine by an analogous reaction.

6th. Messrs. Fittig and Tollens have recently obtained the homologues of benzine, etc., by heating a mixture of brominated benzine and bromide of methyl, ethyl, or amyl, with sodium.

$$\underset{\text{Brominated benzine.}}{\left(\mathrm{C^6H^5Br}\right)} + \underset{\text{Bromide of methyl.}}{\left(\mathrm{CH^3Br}\right)} + \underset{\text{Sodium.}}{\left.\begin{matrix}\mathrm{Na}\\\mathrm{Na}\end{matrix}\right\}} = \underset{\text{Bromide of sodium.}}{2\left(\left.\begin{matrix}\mathrm{Na}\\\mathrm{Br}\end{matrix}\right\}\right)} + \underset{\text{Toluene.}}{\left(\mathrm{C^7H^8}\right)}$$

PROPERTIES.—Only benzine and toluene have been carefully studied. These hydrocarbides have different properties, and require to be examined separately.

1st. Benzine boils at 82°, and is solidified at $-5°$. It is a hexatomic radicle, capable of uniting directly with 2, 4, or 6 atoms of chlorine or bromine. The products of this combination in presence of alcoholic solution of potash lose half their chlorine or bromine in the state of hydrochloric or hydrobromic acid.

Benzine does not combine with hydrochloric or hydriodic acids; the experiment has not been tried with hydrobromic acid, but the result would doubtless be the same.

Submitted to the action of nitric acid, benzine exchanges one atom of hydrogen for one atom of hyponitride. The product formed has received the name of nitro-benzine:

$$\begin{array}{ccccccc} (C^6H^6) & + & (NHO^3) & = & (H^2O) & + & (C^6H^5(NO^2)) \\ \text{Benzine.} & & \text{Nitric acid.} & & \text{Water.} & & \text{Nitrobenzine.} \end{array}$$

2nd. Toluene boils at 111°, and has not as yet been solidified. It never combines directly either with chlorine or bromine; in presence of these metalloids it only gives rise to phenomena of substitution. Neither does it combine with hydracids.

3rd. Monochlorinated toluene ($C^7H^7Cl$) is identical with the chloride of benzyl (*see* Alcohol). M. Cannizzaro has shown that, under the influence of acetate of silver, this body exchanges Cl for ($C^2H^3O^2$), and furnishes a product which gives benzilic alcohol when saponified by potash.

Nevertheless, M. Beilstein has recently shown that there exists a second monochlorinated toluene ($C^7H^7Cl$), differing from the chloride of benzyl, and in which the chlorine is replaced with difficulty. Kékulé explains this fact by considering toluene as methyl-benzine, and by admitting that in the chloride of benzyl the substitution affects the methyl group, while in monochlorinated toluene it affects the phenyl group. The formulæ of these bodies then are:

$$\begin{array}{cc} (C^5H^5.CH^2Cl) & (C^6H^4Cl.CH^3) \\ \text{Chloride of benzyl.} & \text{Monochlorinated toluene.} \end{array}$$

4th. Bichlorinated toluene, heated with mercuric oxide, gives benzoic aldehyd:

$$\begin{array}{ccccccc} \left(C^7H^6Cl^2\right) & + & \left(HgO\right) & = & \left(C^7H^6O\right) & + & \left(Hg''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right) \\ \text{Bichlorinated toluene.} & & \text{Oxide of mercury.} & & \text{Benzoic aldehyd.} & & \text{Mercuric chloride.} \end{array}$$

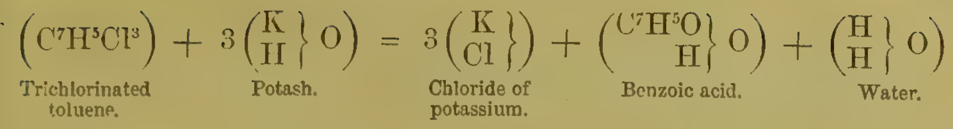
It is nevertheless not identical, as my experiments have shown, with a chloride of the same composition which is obtained by causing benzoic aldehyd to act on the perchloride of phosphorus.

It is conceived that three bichlorinated toluenes may exist, the formulæ of which would be

$$(C^6H^5CHCl^2),\ (C^6H^3Cl^2CH^3),\ \text{and}\ (C^6H^4ClCH^2Cl).$$

The first of these formulæ is that of chlorobenzol and the last that of bichlorinated toluene which is known.

5th. When trichlorinated toluene is submitted to the action of alkalies in alcoholic solution, it exchanges 2Cl for O, and Cl for (OH), and gives chloride of potassium, benzoic acid, and water (Naquet):



$$\underset{\text{Trichlorinated toluene.}}{(C^7H^5Cl^3)} + \underset{\text{Potash.}}{3\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Chloride of potassium.}}{3\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)} + \underset{\text{Benzoic acid.}}{\left(\left.\begin{matrix}C^7H^5O\\H\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

The number of possible trichlorinated toluenes is four:

$(C^6H^5CCl^3)$, $(C^6H^4ClCHCl^2)$, $(C^6H^3Cl^2CH^2Cl)$, and $(C^6H^2Cl^3CH^3)$

6th. Submitted to the influence of nitric acid, toluene is converted into nitro-toluene:

$$\underset{\text{Toluene.}}{(C^7H^8)} + \underset{\text{Nitric acid.}}{(NHO^3)} = \underset{\text{Nitro-toluene.}}{(C^7H^7(NO^2))} + \underset{\text{Water.}}{(H^2O)}$$

Nomenclature.—In this series the following are actually known:

| | |
|---|---|
| Benzine . . . . . . . . . . . . . . | $C^6H^6$ |
| Toluene . . . . . . . . . . . . . . | $C^7H^8$ |
| Xylene and an isomer of this body, ethyl-benzine | $C^8H^{10}$ |
| Cumene . . . . . . . . . . . . . . | $C^9H^{12}$ |
| Cymene . . . . . . . . . . . . . . | $C^{10}H^{14}$ |
| Amyl-benzine . . . . . . . . . . . . | $C^{11}H^{16}$ |

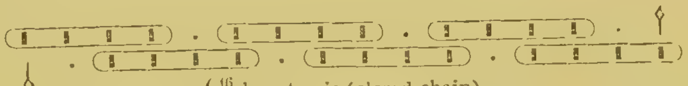
SCHOOL OF MEDICINE

Several hydrocarbides which appear very different have been included under the names of cumene and cymene, but they have been very little studied. It is known that by causing dehydrating agents to act on acetone, a compound is obtained which has been recognized as isomeric with cumene, and which is called mesitylene. Besides these six hydrocarbides, there exists a seventh according to M. Carius; its formula would be $(C^5H^4)$, and M. Carius proposes calling it pentene.

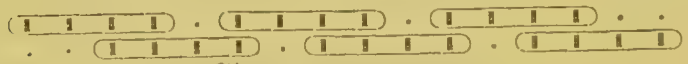
Constitution of the Hydrocarbides having the general Formula $C^nH^{2n-6}$.—Recent experiments made by Messrs. Fittig and Tollens have shown that all the known hydrocarbides of this series are derived directly from benzine $(C^6H^6)$ by the substitution of ethyl, methyl, or amyl for the hydrogen of this body. Thus toluene is methylated benzine. It is supposed that according as several atoms of hydrogen are replaced in benzine by methyl, or one single atom of hydrogen by alcoholic radicles containing more carbon than methyl, isomeric hydrocarbides may be obtained. In fact, ethyl-benzine $(C^6H^5C^2H^5)$, obtained by causing sodium to act on a mixture of brominated benzine and bromide of ethyl, differs from the natural xylene $(C^8H^{10})$ which Messrs. Fittig and Tollens have prepared by heating sodium with a mixture of bromide of methyl and monobrominated toluene.

In order to understand the constitution of the aromatic hydrocarbides, that of benzine must therefore first be determined.

M. Kékulé, in a recent theory on phenols, of which we shall speak presently, admits that benzine represents a closed chain, composed of six atoms of carbon, each of which would be joined to one of its neighbours by two affinities, and to the other by one. Thus a free affinity would remain on each atom, the group $C^6$ would be hexatomic, and benzine ($C^6H^6$) would be saturated. Sometimes the chain might open, and the group $C^6$ would become octoatomic; the open and closed chain would be thus represented:



$C^6$ hexatomic (closed chain).



$C^6$ Octoatomic (open chain).

M. Kékulé has observed, that on acting on aromatic compounds, whose constitution cannot be doubted, oxidizing bodies replace each lateral chain by the group ($CO^2H$), giving acids the basicity of which is equal to the number of lateral chains which the original compound contained; he thence deduced a method of determining the constitution of these bodies when it is not known. Thus cumene ($C^9H^{12}$) is reduced by oxidation into benzoic acid, which is monobasic. Cumene, therefore, contains a single lateral chain, and its formula is ($C^6H^5,C^3H^7$). Cymene ($C^{10}H^{14}$) by slow oxidation gives toluic acid ($C^8H^8O^2$), which is monobasic, and by a more active oxidation it gives terephthalic acid ($C^8H^6O^4$), which is biatomic and bibasic. Cymene, therefore, like toluic acid, contains two lateral chains, and the formula of the first of these bodies is $\left(C^6H^4\begin{cases}CH^3\\C^3H^7\end{cases}\right)$, that of the second being $\left(C^6H^4\begin{cases}CH^3\\CO^2H\end{cases}\right)$. The formula of terephthalic acid is $\left(C^6H^4\begin{cases}CO^2H\\CO^2H\end{cases}\right)$.

M. Kékulé founds his opinion on several important arguments, the first of which is that benzine has not any inferior homologues. In fact, if benzine has the constitution supposed, it cannot have any homologues, for when an atom of carbon is taken from it the group $C^5$ is obtained, which group would have the same atomicity as the $C^6$ group, and would consequently give the hydrocarbides ($C^5H^6$) or ($C^5H^8$), according to whether the chain was open or closed, which hydrocarbides would not be homologues of benzine; moreover, M. Kékulé remarks, that almost all the most complicated aromatic compounds may be finally reduced into benzine; which fact, with the syntheses of Messrs. Fittig and Tollens, shows that benzine is the pivot of all these compounds. Thus if the grouping which constitutes benzine remains, so to speak, intact in all these compounds, it may be supposed that carbon is there grouped differently to what it is in the molecules of methyl, ethyl, or amyl, which are added to this group to form more complicated bodies.

Lastly, M. Kékulé's hypothesis explains some very important isomerisms, which previously could not be accounted for.

Nevertheless there is a fact of which this theory does not take cognizance: benzine can fix 6 atoms of chlorine or bromine, and give the compounds ($C^6H^6Cl^6$) and ($C^6H^6Br^6$); it must, therefore, be admitted that the hexatomic group $C^6$ is transformed, under the influence of chlorine or bromine, into a dodecatomic group ($C^6H^6$), where the atoms will be grouped as in the series $C^nH^{2n}$. This hypothesis is not so simple as that which considers benzine as a hexatomic radicle, containing the dodecatomic group $C^6$ half saturated.

A second fact of which the theory of M. Kékulé does not take notice, is the existence of pentene ($C^5H^4$), supposing that this group really exists, which is as yet doubtful.

In order to smooth this difficulty, M. Wurtz has proposed to replace benzine by pentene as the pivot of the aromatic compounds. Benzine would then be methyl-pentene ($C^5H^3,CH^3$), etc. We might thus account for the fact that in aromatic compounds the substitution of the group ($NO^2$) for H never affects more than 3 atoms. This substitution would in reality affect the group ($C^5H^3$), which has only 3H. Unfortunately the theory thus modified would not take into account either the oxidation of aromatic substances or the properties of benzine, which are so different from those of its higher homologues.

Perhaps there may be two parallel series, one having pentene ($C^5H^4$) for pivot, the other benzine ($C^6H^6$). In this case the benzine known would not be methyl-pentene, and this latter body, isomeric with it, would remain to be discovered.

However it may be, M. Kékulé's theory cannot, as yet, be accepted as certain; it requires further proofs; but as it explains facts which without it are inexplicable, it may be so far accepted until it is either perfectly demonstrated or completely controverted.

**Hydrocarbides having the Formula $C^nH^{2n-8}$.**—In this series only phenylene ($C^6H^4$), cinnamene ($C^8H^8$), and an isomer of this latter body, metastyrol, are known; phenylene having scarcely been studied, we can only speak here of cinnamene and its isomer.

PREPARATION.—Cinnamene is obtained by submitting a mixture of one part of cinnamic acid and four parts of oxide of barium to distillation:

$$\underset{\text{Cinnamic acid.}}{(C^9H^8O^2)} + \underset{\text{Oxide of barium.}}{(BaO)} = \underset{\text{Cinnamene.}}{(C^8H^8)} + \underset{\text{Carbonate of barium.}}{(CBaO^3)}$$

It is also prepared by distilling storax with water charged with carbonate of sodium. When heated to 200°, it is converted into a solid polymer, metastyrol. This latter, submitted to distillation, re-forms cinnamene. It was believed for a long time that cinnamene prepared by means of storax, and to which the name of styrol was given, was isomeric with that obtained by means of cinnamic acid. But this was an error. These two products are identical.

PROPERTIES.—Cinnamene is attacked by bromine and chlorine, and forms a bibromide and a bichloride ($C^8H^8Br^2$) and ($C^8H^8Cl^2$). These new bodies treated by alcoholic solution of potash appear to lose ($HCl$) or ($HBr$), and leave chlorinated or brominated cinnamene; cinnamene ought therefore to be regarded as a biatomic radicle. Laurent states that he has obtained a hexachloride of bichlorinated cinnamene ($C^8H^6Cl^2Cl^6$). This fact requires confirmation; if it be verified, we shall be obliged to admit the hexatomicity of this radicle.

Metastyrol is solid, it reacts with great difficulty on bromine, and evidently has a formula a multiple of ($C^8H^8$), but this formula has not yet been determined. All these hydrocarbides submitted to the action of nitric acid give rise to nitrogenized derivatives.

**Hydrocarbides having the Formula** ($C^nH^{2n-10}$).—Only one hydrocarbide ($C^{26}H^{42}$), which has been little studied, is as yet known in this series. It is prepared by dehydrating cholesterine. It is probable that another would be obtained by heating brominated cinnamene with ethylate of sodium.

**Hydrocarbides having the Formula** $C^nH^{2n-12}$. — Only naphthalin and its isomers belong to this series.

Naphthalin is a solid hydrocarbide which is accidentally produced in the manufacture of coal-gas; it is perfectly colourless, and has an odour of tar; its taste is bitter and aromatic; its density is 1·153 at 18°. When sublimed or when dissolved in alcohol it is obtained crystallized in very thin rhombic plates; but when its ethereal solution is left in a vessel partially covered to retard the evaporation, its crystals are very transparent and much more voluminous.

Naphthalin unites directly with four atoms of chlorine or bromine: above this term these metalloids only give rise to products of substitution; the tetrachloride and tetrabromide of naphthalin are therefore saturated, and we have reason to suppose that if hydrogen were substituted for the chlorine or bromine, the carbide of hydrogen ($C^{10}H^{12}$) which would be obtained would also be saturated.

According to M. Chancel, the dry distillation of benzoate of calcium produces two isomers of naphthalin. Up to the present time a quantity of these bodies sufficient to determine their properties has not been obtained, and their capacity for saturation is not known.

**Hydrocarbides having the Formula** $C^nH^{2n-16}$. — Stilbene ($C^{14}H^{12}$), which is prepared by distilling sulphuretted benzoic aldehyd, is placed in this series.

Excepting the hydrocarbides of these series, none are known with certainty. It is true that a compound has been spoken of which would answer to the formula ($C^{32}H^{32}$), that is to say, to the general formula $C^nH^{2n-32}$, but the existence of such a body is extremely doubtful.

## HYDROCARBON RADICLES.

Each saturated hydrocarbide on losing one, two . . . *n* atoms of hydrogen, gives rise to monatomic, biatomic, etc., radicles. We must study, 1st, free radicles; 2ndly, the products to which they give rise. For greater convenience we will place all these products with the hydrates of these radicles; that is to say, with the alcohols. This study will thus be divided into two parts: 1st, free radicles; 2nd, alcohols. We will, however, study separately the derivatives of these radicles which belong to the ammonia type, and those of their binary compounds which contain metals.

## FREE RADICLES.

**Radicles of uneven Atomicity.**—When the iodides of these radicles are submitted to the action of zinc, iodine is eliminated in the state of iodide of zinc, and a hydrocarbide is liberated:

$$\underset{\text{Iodide of ethyl.}}{2\left(\left.\begin{matrix}C^2H^5\\ I\end{matrix}\right\}\right)} + \underset{\text{Zinc.}}{Zn} = \underset{\text{Iodide of zinc.}}{\left(\left.\begin{matrix}Zn\\ I^2\end{matrix}\right\}\right)} + \left(C^4H^{10}\right)$$

Hydrocarbides identical with the preceding are also obtained when potassic salts of monatomic acids are submitted to electrolysis; only in this case the hydrocarbide obtained is not that which would be given by the iodide derived from the alcohol corresponding to the acid employed, but its second inferior homologue. Thus, while iodide of ethyl gives the hydrocarbide ($C^4H^{10}$), the electrolysis of acetate of potassium furnishes the compound ($C^2H^6$).

$$\underset{\text{Water.}}{(H^2O)} + \underset{\text{Acetate of potassium.}}{2(C^2H^3KO^2)} = \underset{\text{Carbonate of potassium.}}{(CK^2O^3)} + \underset{\text{Hydrogen.}}{H^2} + \underset{\text{Carbonic anhydride.}}{(CO^2)} + C^2H^6$$

Until recently these hydrocarbides were considered as free monatomic radicles. Then, for instance, instead of ($C^4H^{10}$), it was $\left(\left.\begin{matrix}C^2H^5\\ C^2H^5\end{matrix}\right\}\right)$; instead of ($C^2H^6$), $\left(\left.\begin{matrix}CH^3\\ CH^3\end{matrix}\right\}\right)$, corresponding to $\left.\begin{matrix}H\\ H\end{matrix}\right\}$; recent experiments have made the constitution attributed to these compounds doubtful. Their molecule is simple, and they ought to be placed by the side of the hydrocarbides we have studied, of which in this case they would only be physical isomers.

Thus, from this point of view, and supposing that they are not quite identical, free methyl ($C^2H^6$) would be a simple physical isomer of hydride of ethyl; free ethyl ($C^4H^{10}$) would be a physical isomer of hydride of butyl, etc.

Monatomic hydrocarburetted radicles therefore probably do not exist in a free state, and are only found in the groups of compounds whence they are derived.

As yet only two series of monatomic radicles are known; these are:

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FIRST SERIES.

| | |
|---|---|
| Methyl | $C H^3$ |
| Ethyl | $C^2 H^5$ |
| Propyl | $C^3 H^7$ |
| Butyl | $C^4 H^9$ |
| Amyl | $C^5 H^{11}$ |
| Hexyl | $C^6 H^{13}$ |
| Heptyl | $C^7 H^{15}$ |
| Octyl | $C^8 H^{17}$ |
| Nonyl | $C^9 H^{19}$ |
| Decyl | $C^{10}H^{21}$ |
| Undecyl | $C^{11}H^{23}$ |
| Bidecyl | $C^{12}H^{25}$ |
| Tridecyl | $C^{13}H^{27}$ |
| Tetradecyl | $C^{14}H^{29}$ |
| Pentadecyl | $C^{15}H^{31}$ |
| Hexadecyl | $C^{16}H^{33}$ |
| Ceryl | $C^{27}H^{55}$ |
| Myrycyl | $C^{30}H^{61}$ |

SECOND SERIES.

| | |
|---|---|
| Phenyl | $C^6 H^5$ |
| Benzyl | $C^7 H^7$ |
| Tolyl | $C^8 H^9$ |
| Xylenyl | $C^9 H^{11}$ |
| Cumyl | $C^{10}H^{13}$ |

Monatomic radicles of the other series have the same composition as the triatomic radicles we will mention. It is possible that they may differ from these latter by the degree of reciprocal saturation of their carbon. In this case the bodies in which they act as monovalent would be simple non-saturated molecules. The following are known :

| | |
|---|---|
| Formyl | $CH'''$ |
| Acetyl | $C^2H^{3'''}$ |
| Allyl or glyceryl. | $C^3H^{5'''}$ |
| Valeryl | $C^5H^{9'''}$ |
| An unnamed radicle | $C^6H^{11'''}$ |
| Cinnamyl | $C^9H^{9'''}$ |

A very small number of pentatomic radicles are also known ; these are : the radicle $(C^6H^{7v})$ in pinite $\left(\left.\begin{matrix}C^6H^{7v}\\ H^5\end{matrix}\right\} O^5\right)$, and the radicle $(C^{10}H^7)$ which is derived from tetratomic naphthalin by the elimination of H, and the monohydrate of which $\left(\left.\begin{matrix}C^{10}H^{7v}\\ H\end{matrix}\right\} O\right)$ has been recently discovered.

It is possible that the radicle ($C^{10}H^{17}$) of Borneo camphor belongs to this class, but its state of saturation is imperfectly known.

Up to the present time no bodies are known of hydrocarburetted radicles having an uneven atomicity greater than five.

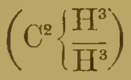
**Radicles of even Atomicity.**—These radicles have the same composition as the non-saturated hydrocarbides whose existence we have theoretically admitted. Are they identical with these hydrocarbides or not? In other words, do they exist in a free state as radicles, that is to say, as non-saturated molecules, or are they hydrocarbides which are saturated when free, and only cease to be so on contact with certain reagents? The question is difficult to decide.

The possibility of the existence of incomplete molecules cannot be doubted; the protochloride of phosphorus, ammonia, oxide of carbon, etc., are certainly molecules of this kind. We do not know whether such molecules exist in the special case of hydrogenized compounds of carbon.

However it may be, supposing that radicles of even atomicity do not exist any more than those of uneven atomicity, in an isolated state, their compounds will be easily formed by means of the hydrocarbides which, according to this hypothesis, would be their isomers.

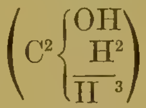
## ALCOHOLS.

Alcohols are bodies which are derived from a fundamental hydrocarbide by the substitution of hydroxyl for hydrogen.



$$\left(C^2\left\{\begin{matrix}H^3\\ \hline H^3\end{matrix}\right.\right)$$

Hydride of ethyl.



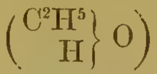
$$\left(C^2\left\{\begin{matrix}OH\\ H^2\\ \hline H^3\end{matrix}\right.\right)$$

Alcohol.

The hydrogen of hydroxyl being only united to the carbon by means of oxygen, it may be said that the oxygen joins an atom of hydrogen to the group ($C^2H^5$), and that alcohol is a hydrate of this latter radicle.

$(C^2H^5)$

Ethyl.



$$\left(\begin{matrix}C^2H^5\\ H\end{matrix}\right\}O\Big)$$

Hydrate of ethyl
(alcohol).

It is very evident that both these formulæ of alcohol expressing the same fact, are useful, and that either one or the other may be chosen according to circumstances.

There are alcohols which result from the substitution of a single atom of hydroxyl for H, these are called monatomic; others which result from the substitution of two, three . . . *n* atoms of hydroxyl for H, and are called bi, tri, *n* atomic. Alcohols are known whose atomicity rises as high as six.

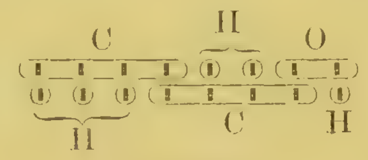
## MONATOMIC ALCOHOLS.

Monatomic alcohols contain a single atom of typical hydrogen, which may be replaced, either by the radicle of the alcohol itself, in which case an ether, properly so called, is produced; or by the radicle of another alcohol, when a mixed ether is formed; or, again, by an acid radicle, in which case a compound ether is produced.

Moreover, these alcohols can exchange the group (OH) for chlorine, bromine, iodine, or fluorine, and give rise to the simple ethers.

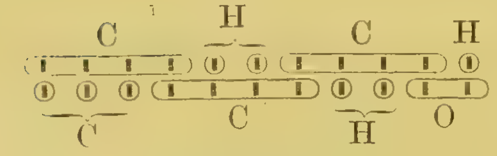
It may therefore be stated that, if alcohols are the hydrates of hydrocarbides, the ethers proper are the anhydrides of these hydrocarbides; mixed ethers are the double anhydrides; simple ethers the haloid salts, and compound ethers the oxygenated salts.

Monatomic alcohols are divided into primary, secondary, tertiary, etc., alcohols, according to the manner in which their different atoms of carbon are united. If the atoms of carbon are united in such a manner that those in the centre exchange two affinities with the adjoining atoms of carbon, and those on the outside only one, they are primary alcohols. Thus ethylic, propylic, etc., alcohols—



$$= \left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O$$

Ethylic alcohol.

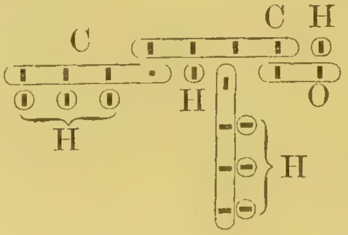


$$= \left.\begin{matrix}C^3H^7\\H\end{matrix}\right\}O$$

Propylic alcohol.

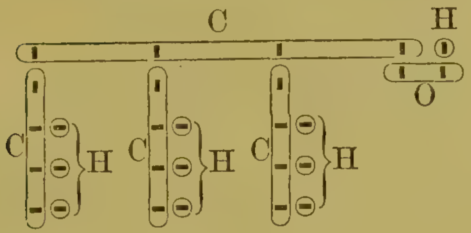
are primary alcohols.

If in a primary alcohol H be replaced by the radicle methyl ($CH^3$), a secondary alcohol is obtained; if two atoms of H be replaced by two atoms of methyl, a tertiary radicle is obtained, and so on. Thus the isopropylic alcohol—



$$= \left.\begin{matrix}C^2H^4(CH^3)\\H\end{matrix}\right\}O$$

is a secondary alcohol, and the trimethylated methylic alcohol—



$$= C \left\{ \begin{matrix} CH^3 \\ CH^3 \\ CH^3 \\ OH \end{matrix} \right.$$

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is a tertiary alcohol.

Only primary, secondary, and tertiary alcohols are known as yet; the primary alcohols are much the best known and the most important.

## PRIMARY MONATOMIC ALCOHOLS.

Preparation.—Primary monatomic alcohols may be obtained either by means of the corresponding saturated hydrocarbides, or of carburetted hydrogens which are radicles of uneven atomicity, or of aldehyds, or finally of glycols.

*First Method.*—In order to prepare alcohols by means of saturated hydrocarbides, these are treated by chlorine or bromine. A monochlorinated or monobrominated product of substitution is obtained which is identical with the chloride or bromide of the corresponding alcohol radicle. This product, submitted to the action of the acetate of silver or of potassium, furnishes acetic ether (the acetate of the alcohol radicle), and acetic ether, treated by potash, is resolved into acetate of potassium and alcohol:

$$\text{1st.}\quad \underset{\substack{\text{Hydride}\\\text{of methyl.}}}{\left(CH^4\right)} + \underset{\text{Chlorine.}}{\left.\begin{matrix} Cl \\ Cl \end{matrix}\right\}} = \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{\left(\left.\begin{matrix} H \\ Cl \end{matrix}\right\}\right)} + \underset{\substack{\text{Chloride of}\\\text{methyl.}}}{\left(\left.\begin{matrix} CH^3 \\ Cl \end{matrix}\right\}\right)}$$

$$\text{2nd.}\quad \underset{\substack{\text{Chloride of}\\\text{methyl.}}}{\left(\left.\begin{matrix} CH^3 \\ Cl \end{matrix}\right\}\right)} + \underset{\text{Acetate of silver.}}{\left(\left.\begin{matrix} C^2H^3O \\ Ag \end{matrix}\right\} O\right)} = \underset{\substack{\text{Acetate of}\\\text{methyl.}}}{\left(\left.\begin{matrix} CH^3 \\ C^2H^3O \end{matrix}\right\} O\right)} + \underset{\substack{\text{Chloride}\\\text{of silver.}}}{\left(\left.\begin{matrix} Ag \\ Cl \end{matrix}\right\}\right)}$$

$$\text{3rd.}\quad \underset{\text{Acetate of methyl.}}{\left(\left.\begin{matrix} CH^3 \\ C^2H^3O \end{matrix}\right\} O\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix} K \\ H \end{matrix}\right\} O\right)} = \underset{\substack{\text{Acetate of}\\\text{potassium.}}}{\left(\left.\begin{matrix} C^2H^3O \\ K \end{matrix}\right\} O\right)} + \underset{\substack{\text{Methylic}\\\text{alcohol.}}}{\left(\left.\begin{matrix} CH^3 \\ H \end{matrix}\right\} O\right)}$$

*Second Method.*—The carburetted hydrogens which act as radicles of even atomicity may unite, according to their capacity for saturation, with one or several molecules of hydrochloric, hydrobromic, or hydriodic acid. If they are combined with a single molecule of these acids, bodies are obtained which are afterwards transformed into alcohols by the successive action of acetate of silver and of potassium, as in the preceding case:

$$\underset{\text{Ethylene.}}{\left(C^2H^{4''}\right)} + \underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\text{Chloride of ethyl.}}{\left(C^2H^5Cl\right)}$$

M. Berthelot, to whom we owe the discovery of this process, believed it to be general. But M. Wurtz has since found that this is not the case. Ordinary alcohol alone can be prepared in this manner; in all other cases isomers of the true alcohols are obtained (*see* Pseudo-alcohols).

These hydrocarbides may also be transformed into alcohols by combining them with concentrated sulphuric acid and then distilling the product with water:

1st. $$\underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Ethylene.}}{\left(C^2H^{4''}\right)} = \underset{\text{Ethyl-sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2''}\\C^2H^5\\H\end{matrix}\right\}O^2\right)}$$

2nd. $$\underset{\text{Ethyl-sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2''}\\C^2H^5\\H\end{matrix}\right\}O^2\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)}$$

This method also appears to give pseudo-alcohols, except in the cases of ordinary and propylic alcohols. It is less general than the preceding one. Sulphuric acid, in fact, modifies certain hydrocarbides, and transforms them into polymers, on which it has no action.

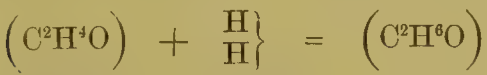
*Third Method.*—Alcohols may be prepared from the aldehyds by two processes.

The first consists in causing alcoholic solution of potash to act on the aldehyd; a potassic salt of the acid corresponding to this aldehyd is formed, and the alcohol of the same series:

$$\underset{\text{Benzoic aldehyd.}}{2\left(C^7H^6O\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Benzoate of potassium.}}{\left(\left.\begin{matrix}C^7H^5O\\K\end{matrix}\right\}O\right)} + \underset{\text{Benzilic alcohol.}}{\left(\left.\begin{matrix}C^7H^7\\H\end{matrix}\right\}O\right)}$$

This method can only be applied to the alcohols derived from hydrocarbides of the general formula $C^nH^{2n-6}$ (aromatic series); however, by modifying it a little, and replacing alcoholic potash by slaked lime, M. Fittig has transformed œnanthylic aldehyd ($C^7H^{14}O$) into heptylic alcohol ($C^7H^{16}O$), and valeric aldehyd ($C^5H^{10}O$) into amylic alcohol ($C^5H^{12}O$).

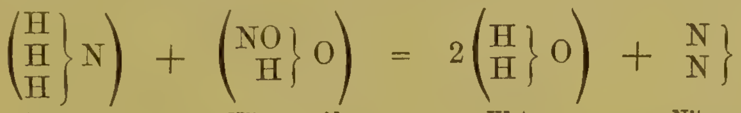
The second process consists in causing nascent hydrogen, developed by means of sodium amalgam, to act on the aldehyds. It succeeds not only with aldehyds, but also with the isomers of these bodies. Thus ordinary alcohol is obtained by causing nascent hydrogen to act either on the aldehyd or on its isomer, the oxide of ethylene:



$$\left(C^2H^4O\right) + \left.\begin{matrix}H\\H\end{matrix}\right\} = \left(C^2H^6O\right)$$

Aldehyd, or oxide of ethylene. Hydrogen. Alcohol.

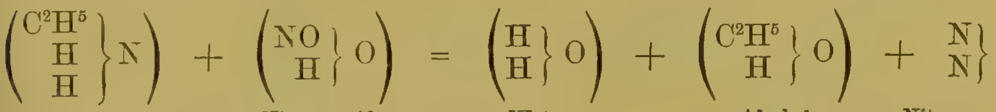
*Fourth Method.*—When ammonia is treated by nitrous acid, water and free nitrogen are obtained:



$$\left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right) + \left(\left.\begin{matrix}NO\\H\end{matrix}\right\}O\right) = 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + \left.\begin{matrix}N\\N\end{matrix}\right\}$$

Ammonia. Nitrous acid. Water. Nitrogen.

Now, supposing an atom of the hydrogen of the ammonia to be replaced by a radicle of alcohol, as takes place in the compound ammonias, it is evident that one of the two molecules of water which form in the reaction would have one of its atoms of hydrogen replaced by the same radicle:

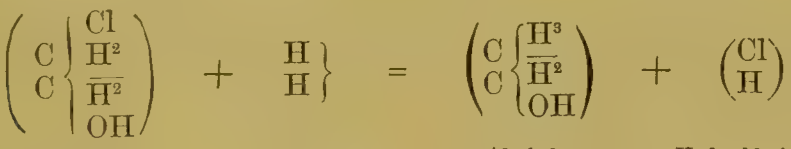


$$\left(\left.\begin{matrix}C^2H^5\\H\\H\end{matrix}\right\}N\right) + \left(\left.\begin{matrix}NO\\H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right) + \left.\begin{matrix}N\\N\end{matrix}\right\}$$

Ethylamine. Nitrous acid. Water. Alcohol. Nitrogen.

In this case the alcohol obtained is transformed into nitrous ether on contact with the excess of nitrous acid, and the operation must be completed by decomposing the ether thus formed by potash.

*Fifth Method.*—Monatomic alcohols are also obtained from the glycols. On submitting the monochlorhydrins of these bodies to the action of nascent hydrogen, the chlorine is replaced by hydrogen, and the alcohol sought for is formed:



$$\left(\begin{matrix}C\\C\end{matrix}\left|\begin{matrix}Cl\\H^2\\\overline{H^2}\\OH\end{matrix}\right.\right) + \left.\begin{matrix}H\\H\end{matrix}\right\} = \left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\\overline{H^2}\\OH\end{matrix}\right.\right) + \left(\begin{matrix}Cl\\H\end{matrix}\right)$$

Monochlorhydrin of glycol. Hydrogen. Alcohol. Hydrochloric acid.

PROPERTIES.—1st. *Action of Oxidants.*—Under the influence of oxidizing agents, all the alcohols are capable of losing two atoms of H which are not replaced. The bodies thus produced are called aldehyds. The alcohols can also exchange $H^2$ for O, and produce acids.

(1). $2(C^2H^6O) + O^2 = 2(H^2O) + 2(C^2H^4O)$
Alcohol. Oxygen. Water. Aldehyd.

(2.) $(C^2H^6O) + O^2 = (H^2O) + (C^2H^4O^2)$
Alcohol. Oxygen. Water. Acetic acid.

2nd. *Action of Dehydrants.*—Under the influence of dehydrating agents, alcohols lose $(H^2O)$ and give rise to a hydrocarbide:

$(C^2H^6O) = (H^2O) + (C^2H^4)$
Alcohol. Water. Ethylene.

Two atoms of alcohol can also lose ($H^2O$) and be transformed into an ether proper:

$$\underset{\text{Alcohol.}}{2(C^2H^6O)} = \underset{\text{Water.}}{(H^2O)} + \underset{\text{Ether.}}{(C^4H^{10}O)}$$

These reactions are well marked only in the series of alcohols which correspond to the hydrocarbides $C^nH^{2n+2}$ (the fatty series).

3rd. *Action of Chlorides, Bromides, and Iodides of Phosphorus.*—When treated by the chloride, bromide, or iodide of phosphorus, they lose the residue (HO) for which Cl, Br, or I, is substituted; thus, a chloride, bromide, or iodide of the radicle of the alcohol is produced, along with phosphorous or phosphoric acid, according as proto or perchloride, or bromide have been employed, and the hydracid of chlorine, bromine, or iodine:

$$\underset{\text{Alcohol.}}{4\left(\left.\begin{matrix}C^2H^5\\ H\end{matrix}\right\}O\right)} + \underset{\text{Perchloride of phosphorus.}}{\left(PCl^5\right)} = \underset{\text{Chloride of ethyl.}}{4\left(\left.\begin{matrix}C^2H^5\\ Cl\end{matrix}\right\}\right)} + \underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\ Cl\end{matrix}\right\}\right)} + \underset{\text{Phosphoric acid.}}{\left(\left.\begin{matrix}PO'''\\ H^3\end{matrix}\right\}O^3\right)}$$

In reality, this reaction has two stages, as the following equations show:

FIRST STAGE.

$$\underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\ H\end{matrix}\right\}O\right)} + \underset{\text{Perchloride of phosphorus.}}{\left(PCl^5\right)} = \underset{\text{Oxychloride of phosphorus.}}{\left(PCl^3O\right)} + \underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\ Cl\end{matrix}\right\}\right)} + \underset{\text{Chloride of ethyl.}}{\left(\left.\begin{matrix}C^2H^5\\ Cl\end{matrix}\right\}\right)}$$

SECOND STAGE.

$$\underset{\text{Alcohol.}}{3\left(\left.\begin{matrix}C^2H^5\\ H\end{matrix}\right\}O\right)} + \underset{\text{Oxychloride of phosphorus.}}{PCl^3O} = \underset{\text{Phosphoric acid.}}{\left(\left.\begin{matrix}PO'''\\ H^3\end{matrix}\right\}O^3\right)} + \underset{\text{Chloride of ethyl.}}{3\left(\left.\begin{matrix}C^2H^5\\ Cl\end{matrix}\right\}\right)}$$

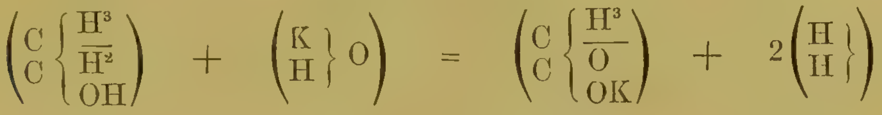
4. *Action of Acids.*—When treated by acids at a temperature varying according to the strength of these latter, double decomposition takes place, and water and a compound ether are formed:

$$\underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\ H\end{matrix}\right\}O\right)} + \underset{\text{Acetic acid.}}{\left(\left.\left(\begin{matrix}C^2H^3O\\ H\end{matrix}\right)\right\}O\right)} = \underset{\text{Acetic ether (acetate of ethyl).}}{\left(\left.\begin{matrix}C^2H^3O\\ C^2H^5\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)}$$

These ethers being decomposed by water, it always happens that there is a moment in these reactions when the decomposing action of the water formed neutralizes the opposite action of the affinities of the acid and alcohol. The action is then arested, though the mixture still contains a certain proportion of acid and alcohol, which remain free. M. Berthelot thence concludes that, nothing of the kind being produced in the action of acids on bases, the compound ethers cannot be compared to salts. This conclusion cannot be accepted. The phenomenon in question is owing to the respective affinities of the bodies of which we speak, and not to the constitution of the compounds which are formed; it is probable that if, instead of causing strong acids to act on potash, weak acids were made to act on the hydrated oxides of tin or antimony, phenomena analogous to those observed with the alcohols would be obtained.

A simple or compound ether is produced, according to whether the acid acting on an alcohol be a hydracid or an oxyacid.

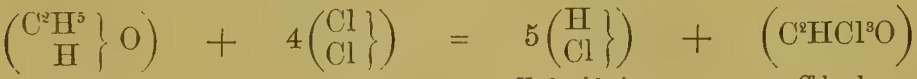
5th. *Action of Alkalies on the Alcohols.*— Under the influence of fused potash, the alcohols disengage hydrogen and give the potassic salt of the acid which corresponds to them.



$$\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\\hline H^2\\OH\end{matrix}\right.\right) + \left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right) = \left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\\hline O\\OK\end{matrix}\right.\right) + 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}\right)$$

Alcohol. Potash. Acetate of potassium. Hydrogen.

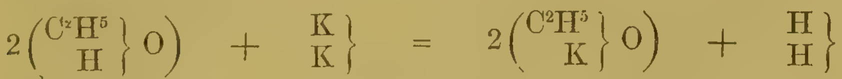
6th. *Action of the Halogen Metalloids.*—The alcohols when submitted to the influence of chlorine or bromine first lose two atoms of hydrogen which are not replaced. The other atoms of hydrogen are then replaced by these metalloids. All may be replaced except one, which is probably the typical hydrogen of the alcohol:



$$\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right) + 4\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}\right) = 5\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right) + \left(C^2HCl^3O\right)$$

Alcohol. Chlorine. Hydrochloric acid. Chloral.

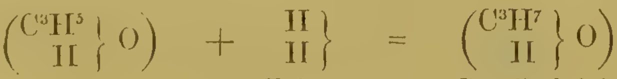
7th. *Action of the Alkaline Metals.*—The alkaline metals react strongly on monatomic alcohols, disengaging hydrogen and being themselves substituted for the hydrogen eliminated:



$$2\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right) + \left.\begin{matrix}K\\K\end{matrix}\right\} = 2\left(\left.\begin{matrix}C^2H^5\\K\end{matrix}\right\}O\right) + \left.\begin{matrix}H\\H\end{matrix}\right\}$$

Alcohol. Potassium. Ethylate of potassium. Hydrogen.

8th. *Action of Hydrogen.*—Many alcohols belonging to less hydrogenized series than that expressed by the general formula $C^nH^{2n+2}O$ can combine with nascent hydrogen and pass to the state of more hydrogenized alcohols of another series. Allylic and probably cinnamic alcohol present this characteristic.



$$\left(\left.\begin{matrix}C^3H^5\\H\end{matrix}\right\}O\right) + \left.\begin{matrix}H\\H\end{matrix}\right\} = \left(\left.\begin{matrix}C^3H^7\\H\end{matrix}\right\}O\right)$$

Allylic alcohol. Hydrogen. Propylic alcohol.

These alcohols appear also to be capable of uniting directly with bromine, at least M. Reboul has stated that their ethers possess this property.

### ETHERS OF THE PRIMARY ALCOHOLS.

We have seen that the name ether has been given to a series of bodies which arise from the substitution either of an acid or of an alcohol radicle for the atom of typical hydrogen these alcohols contain, or from the substitution of a halogen metalloid for the hydroxyl of the alcohols. We will divide the ethers into two large classes—those which contain acid radicles and those which do not.

**Ethers containing Acid Radicles.**—These may be divided into simple and compound ethers.

SIMPLE ETHERS.—*Preparation.*—These are easily prepared, either by causing the hydracids of chlorine, bromine, or iodine, to act on the alcohols, or by treating the latter by the chlorides, bromides, or iodides of phosphorus. They may also be obtained by substituting the chlorine or bromine for hydrogen in the fundamental hydrocarbide of the series. The hydrocyanic ethers are obtained by double decomposition, on causing cyanide of potassium to act on hydrochloric ethers, or on the potassic salts of acid ethers.

$$\left(\left.\begin{matrix}K\\ CN\end{matrix}\right\}\right) + \left(\left.\begin{matrix}SO^{2\prime\prime}\\ C^5H^{11}\\ K\end{matrix}\right\} O^2\right) = \left(\left.\begin{matrix}SO^{2\prime\prime}\\ K^2\end{matrix}\right\} O^2\right) + \left(\left.\begin{matrix}C^5H^{11}\\ CN\end{matrix}\right\}\right)$$

Cyanide of potassium. Amyl-sulphate of potassium. Sulphate of potassium. Cyanide of amyl.

PROPERTIES.—α. Simple ethers, treated with zinc, give a haloid salt of zinc and a combination of zinc with the alcohol radicle. This latter body, in presence of a fresh quantity of the simple ether, liberates a hydrocarbide, which hitherto has been considered as the radicle of the alcohol, but which has perhaps quite another constitution. (*See* Hydrocarburetted Radicles.)

$$2\left(\left.\begin{matrix}C^2H^5\\ I\end{matrix}\right\}\right) + 2Zn = \left(\left.\begin{matrix}Zn''\\ I^2\end{matrix}\right\}\right) + \left(\left.\begin{matrix}Zn''\\ (C^2H^5)^2\end{matrix}\right\}\right)$$

Iodide of ethyl. Zinc. Iodide of zinc. Ethylide of zinc (zinc-ethyl).

$$\left(\left.\begin{matrix}Zn''\\ (C^2H^5)^2\end{matrix}\right\}\right) + 2\left(\left.\begin{matrix}C^2H^5\\ I\end{matrix}\right\}\right) = \left(\left.\begin{matrix}Zn''\\ I^2\end{matrix}\right\}\right) + \left(C^4H^{10}\right)$$

Zinc-ethyl. Iodide of ethyl. Iodide of zinc.

β. Simple ethers, treated by water and zinc at 200°, give rise to the fundamental hydrocarbide of the series. (*See* Saturated Hydrocarbides.)

γ. Submitted to the action of salts of silver or of potassium, the simple ethers give rise to a double decomposition, in which a metallic haloid salt and a compound ether are produced:

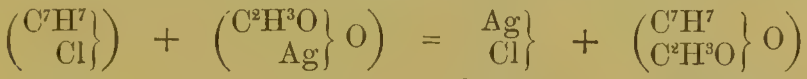
$$\left(\left.\begin{matrix}C^2H^5\\ Cl\end{matrix}\right\}\right) + \left(\left.\begin{matrix}C^2H^3O\\ Ag\end{matrix}\right\} O\right) = \left(\left.\begin{matrix}Ag\\ Cl\end{matrix}\right\}\right) + \left(\left.\begin{matrix}C^2H^3O\\ C^2H^5\end{matrix}\right\} O\right)$$

Chloride of ethyl. Acetate of silver. Chloride of silver. Acetate of ethyl.

Compound Ethers.—*Preparation.*—There are five processes by which these ethers are prepared :

α. The acid is mixed with alcohol. If the acid be strong, the reaction takes place in the cold ; if the acid be weak, the mixture must be heated in sealed tubes, at a temperature which varies with the bodies to be formed.

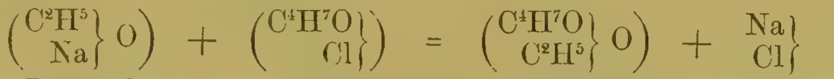
β. A salt of silver is made to act on a simple ether of the alcohol of which a compound ether is to be obtained :



$$\left(\left.\begin{matrix}C^7H^7\\ Cl\end{matrix}\right\}\right) + \left(\left.\begin{matrix}C^2H^3O\\ Ag\end{matrix}\right\} O\right) = \left.\begin{matrix}Ag\\ Cl\end{matrix}\right\} + \left(\left.\begin{matrix}C^7H^7\\ C^2H^3O\end{matrix}\right\} O\right)$$

Chloride of benzile. Acetate of silver. Chloride of silver. Acetate of benzile.

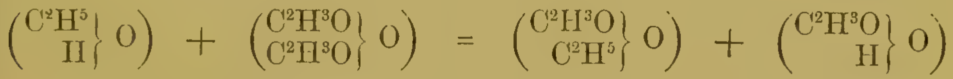
γ. The chloride of an acid radicle is made to act on an alcohol, or on its sodic derivative. Either hydrochloric acid or a metallic chloride is produced, and at the same time a compound ether :



$$\left(\left.\begin{matrix}C^2H^5\\ Na\end{matrix}\right\} O\right) + \left(\left.\begin{matrix}C^4H^7O\\ Cl\end{matrix}\right\}\right) = \left(\left.\begin{matrix}C^4H^7O\\ C^2H^5\end{matrix}\right\} O\right) + \left.\begin{matrix}Na\\ Cl\end{matrix}\right\}$$

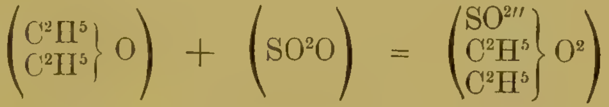
Ethylate of sodium. Chloride of butyryl. Butyrate of ethyl. Chloride of sodium.

δ. An acid anhydride is made to react on an alcohol or on a simple ether :



$$\left(\left.\begin{matrix}C^2H^5\\ H\end{matrix}\right\} O\right) + \left(\left.\begin{matrix}C^2H^3O\\ C^2H^3O\end{matrix}\right\} O\right) = \left(\left.\begin{matrix}C^2H^3O\\ C^2H^5\end{matrix}\right\} O\right) + \left(\left.\begin{matrix}C^2H^3O\\ H\end{matrix}\right\} O\right)$$

Alcohol. Acetic anhydride. Acetate of ethyl. Acetic acid.

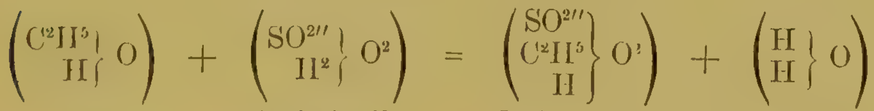


$$\left(\left.\begin{matrix}C^2H^5\\ C^2H^5\end{matrix}\right\} O\right) + \left(SO^2O\right) = \left(\left.\begin{matrix}SO^{2''}\\ C^2H^5\\ C^2H^5\end{matrix}\right\} O^2\right)$$

Ether. Sulphuric anhydride. Neutral sulphate of ethyl.

ε. An acid is made to react on an alcohol in presence of another stronger acid, such as sulphuric or hydrochloric acid. It is probable that there are two stages in these reactions. When sulphuric acid is employed there would be formed, according to this hypothesis, a sulphovinic acid, which on contact with the second acid would re-form the sulphuric acid and give rise to a compound ether :

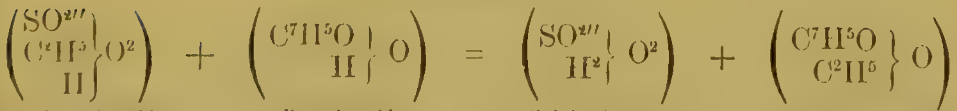
### First Stage.



$$\left(\left.\begin{matrix}C^2H^5\\ H\end{matrix}\right\} O\right) + \left(\left.\begin{matrix}SO^{2''}\\ H^2\end{matrix}\right\} O^2\right) = \left(\left.\begin{matrix}SO^{2''}\\ C^2H^5\\ H\end{matrix}\right\} O^2\right) + \left(\left.\begin{matrix}H\\ H\end{matrix}\right\} O\right)$$

Alcohol. Sulphuric acid. Sulphovinic acid. Water.

### Second Stage.



$$\left(\left.\begin{matrix}SO^{2''}\\ C^2H^5\\ H\end{matrix}\right\} O^2\right) + \left(\left.\begin{matrix}C^7H^5O\\ H\end{matrix}\right\} O\right) = \left(\left.\begin{matrix}SO^{2''}\\ H^2\end{matrix}\right\} O^2\right) + \left(\left.\begin{matrix}C^7H^5O\\ C^2H^5\end{matrix}\right\} O\right)$$

Sulphovinic acid. Benzoic acid. Sulphuric acid. Benzoate of ethyl.

If the sulphuric acid were replaced by hydrochloric, a hydrochloric ether would first be formed, which, on reacting on the oxygenized acid, would re-form the hydrochloric acid and give a compound ether:

FIRST STAGE.

$$\underset{\text{Butylic alcohol.}}{\left(\left.\begin{matrix}C^4H^9\\H\end{matrix}\right\}O\right)} + \underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\text{Chloride of butyl.}}{\left(\left.\begin{matrix}C^4H^9\\Cl\end{matrix}\right\}\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

SECOND STAGE.

$$\underset{\text{Chloride of butyl.}}{\left(\left.\begin{matrix}C^4H^9\\Cl\end{matrix}\right\}\right)} + \underset{\text{Formic acid.}}{\left(\left.\begin{matrix}CHO\\H\end{matrix}\right\}O\right)} = \underset{\text{Formiate of butyl.}}{\left(\left.\begin{matrix}C^4H^9\\CHO\end{matrix}\right\}O\right)} + \underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)}$$

*Compound Ethers formed by means of the Polyatomic Acids.*—Polyatomic acids can always form a number of ethers equal to the number of atoms of typical hydrogen they contain. When this hydrogen is entirely replaced by an alcohol radicle, the ether formed is neutral; but when it is only partially replaced, acid ethers are obtained, and the remaining basic hydrogen may be replaced by a metal.

The neutral ethers of these acids are easily procured by the processes we have mentioned.

The acid ethers are generally obtained by gently heating an alcohol with a biatomic acid, saturating the compound by a base which precipitates the excess of acid while forming a soluble salt with the acid ether formed, and then extracting this ether from its salt by precipitating the metal it contains by a suitable acid.

This class of ethers may also be obtained by the incomplete saponification of neutral ethers:

$$\underset{\text{Neutral oxalate of ethyl.}}{\left(\left.\begin{matrix}C^2O^{2\prime\prime}\\(C^2H^5)^2\end{matrix}\right\}O^2\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)} + \underset{\text{Ethyloxalate of potassium.}}{\left(\left.\begin{matrix}C^2O^{2\prime\prime}\\C^2H^5\\K\end{matrix}\right\}O^2\right)}$$

This process is very useful in the preparation of the mono- or bi-acid ethers of triatomic acids.

*Properties of Compound Ethers.*—The compound ethers, when treated with bases, produce a metallic salt, and re-form the alcohol. This double decomposition is called saponification. Water alone saponifies the compound ethers at a high temperature:

$$\underset{\text{Acetic ether.}}{\left(\left.\begin{matrix}C^2H^3O\\C^2H^5\end{matrix}\right\}O\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Acetate of potassium.}}{\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right)} + \underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)}$$

**Ethers which do not contain Acid Radicles.**—These ethers contain two alcohol radicles, united by the intervention of oxygen. When these two radicles are identical, the ether is *an ether proper.* When they differ, the ether is said to be a mixed ether.

ETHERS PROPER.—*Preparation.*—The ether, properly so called, of an alcohol may be obtained by four principal processes:

1*st Process.*—By heating the alcohol with bodies having great affinity for water, such as chloride of zinc. Two molecules of alcohol unite, giving up a molecule of water, and forming the ether:

$$2\underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)} = \underset{\text{Oxide of ethyl (ether).}}{\left(\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

The bodies having a great affinity for water may be replaced by bodies which are almost inert, such as iodide of mercury. These bodies serve as a centre of decomposition, and allow the alcohol to react on itself as it would on an acid.

2*nd Process.*—The alcohol is made to react on a strong polyatomic acid. A series of double decompositions takes place which are analogous to those we spoke of in the fifth method of preparing compound ethers:

FIRST STAGE.

$$\underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)} + \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2\prime\prime}\\H^2\end{matrix}\right\}O^2\right)} = \underset{\text{Sulphovinic acid.}}{\left(\left.\begin{matrix}SO^{2\prime\prime}\\C^2H^5\\H\end{matrix}\right\}O^2\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

SECOND STAGE.

$$\underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)} + \underset{\text{Sulphovinic acid.}}{\left(\left.\begin{matrix}SO^{2\prime\prime}\\C^2H^5\\H\end{matrix}\right\}O^2\right)} = \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2\prime\prime}\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Ether.}}{\left(\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}O\right)}$$

The acid re-formed in the second stage of the reaction recommences the cycle of these transformations. Consequently a relatively small quantity of a polybasic acid can transform almost indefinite quantities of alcohol into ether, the only limit being the formation of secondary products.

This theory of etherification has been verified by Mr. Williamson in the following manner:

He prepared an acid ether of amylic alcohol (amylsulphuric acid); then he transmitted a current of ordinary alcohol through the gently-heated ether. It is evident that if, as the theory supposes, the ether arises from the successive decompositions and recompositions of the acid ether, the portions of this latter body which are found in the apparatus at the end of the operation are not of the same composition as those placed there at the commencement. Consequently, if the theory be correct, in the experiment just mentioned an acid ether ought to be found in the apparatus at the end of the operation, differing from the one originally placed there. This is what actually occurs.

Moreover, during the time the decomposition of the acid ether formed at the commencement lasts, there ought to be disengaged, not ordinary ether, but a mixed ether formed by the radicles of the two alcohols in question: this the experiment also confirms.

The following equations render this reasoning more intelligible:

$$\left(\left.\begin{matrix}SO^{2''}\\C^5H^{11}\\H\end{matrix}\right\}O^2\right) + \left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}C^2H^5\\C^5H^{11}\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)$$

Amyl-sulphuric acid. Alcohol. Oxide of ethyl and of amyl. Sulphuric acid.

$$\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right) + \left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}SO^{2''}\\C^2H^5\\H\end{matrix}\right\}O^2\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

Sulphuric acid. Alcohol. Ethyl-sulphuric acid. Water.

It will be seen that at the commencement the apparatus contains amylsulphuric acid, and at the end ethylsulphuric acid; and also that during the decomposition of the first of these bodies, neither oxide of ethyl nor oxide of amyl are disengaged, but the double oxide of ethyl and amyl.

3rd *Process.*—The third process consists in causing the chloride, bromide, or iodide of an alcohol radicle to react on the sodium derivative of the same alcohol:

$$\left(\left.\begin{matrix}C^2H^5\\Cl\end{matrix}\right\}\right) + \left(\left.\begin{matrix}C^2H^5\\Na\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}Na\\Cl\end{matrix}\right\}\right)$$

Chloride of ethyl. Ethylate of sodium. Ether. Chloride of sodium.

4th *Process.*—The simple ethers are saponified by anhydrous bases:

$$2\left(\left.\begin{matrix}C^2H^5\\Cl\end{matrix}\right\}\right) + (BaO) = \left(\left.\begin{matrix}Ba''\\Cl^2\end{matrix}\right\}\right) + \left(\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}O\right)$$

Chloride of ethyl. Anhydrous oxide of barium. Chloride of barium. Ether.

MIXED ETHERS.—*Preparation.*—These are obtained, either by Mr. Williamson's process, that is to say, by causing a strong polybasic acid to act on a mixture of two alcohols, or by submitting the sodium derivative of an alcohol to the action of the simple ether of a different alcohol.

*Properties of Ethers proper, and of mixed Ethers.*—1st. The two carbonized groups contained in these ethers are so strongly united together by the oxygen that the chlorides of phosphorus can only with great difficulty seize this oxygen and divide the molecule. The protochloride of phosphorus can only act on ordinary ether in a closed tube at a high temperature. The reaction gives phosphorous anhydride and chloride of ethyl:

$$\underset{\text{Ether.}}{3\left(\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}O\right)} + \underset{\text{Protochloride of phosphorus.}}{2(PCl^3)} = \underset{\text{Phosphorous anhydride.}}{(P^2O^3)} + \underset{\text{Chloride of ethyl.}}{6\left(\left.\begin{matrix}C^2H^5\\Cl\end{matrix}\right\}\right)}$$

2nd. Treated by acids or by acid anhydrides with heat, these ethers enter into double decomposition with them, and give, either two molecules of the same compound ether, or two different compound ethers:

$$\underset{\text{Oxide of ethyl and methyl.}}{\left(\left.\begin{matrix}CH^3\\C^2H^5\end{matrix}\right\}O\right)} + \underset{\text{Acetic anhydride.}}{\left(\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O\right)} = \underset{\text{Acetate of methyl.}}{\left(\left.\begin{matrix}C^2H^3O\\CH^3\end{matrix}\right\}O\right)} + \underset{\text{Acetate of ethyl.}}{\left(\left.\begin{matrix}C^2H^3O\\C^2H^5\end{matrix}\right\}O\right)}$$

3rd. Ethylic ether, and probably its homologues, give products of substitution under the influence of chlorine.

M. Malaguti has thus obtained tetrachlorinated ethylic ether, which he has wrongly called bichlorinated ($C^4H^6Cl^4O$), and M. Lieben has prepared the bichlorinated ether, called by him monochlorinated $\left(\left.\begin{matrix}C^2H^4Cl\\C^2H^4Cl\end{matrix}\right\}O\right)$. This latter body, treated in the cold with zinc-ethyl or with zinc-methyl, exchanges Cl for the ethyl or methyl, and gives products which have the formulæ $\left(\left.\begin{matrix}C^2H^4(C^2H^5)\\C^2H^4Cl\end{matrix}\right\}O\right)$ and $\left(\left.\begin{matrix}C^2H^4(CH^3)\\C^2H^4Cl\end{matrix}\right\}O\right)$. These products when heated in a sealed tube with fresh quantities of zinc-methyl or zinc-ethyl exchange their last atom of chlorine for the ethyl or methyl, and furnish the bi-ethylic ether $\left(\left.\begin{matrix}C^2H^4(C^2H^5)\\C^2H^4(C^2H^5)\end{matrix}\right\}O\right)$ or the bi-methylic ether $\left(\left.\begin{matrix}C^2H^4(CH^3)\\C^2H^4(CH^3)\end{matrix}\right\}O\right)$.

By treating the monochlorinated (bichlorinated) ether by ethylate or methylate of sodium, M. Lieben has succeeded in substituting oxethyl or oxymethyl for the chlorine, and has thus obtained:

| | |
|---|---|
| Chloroxethylic ether . . . . | $\left(\left.\begin{matrix}C^2H^4(C^2H^5O)\\C^2H^4Cl\end{matrix}\right\}O\right)$ |
| Dioxethylic ether . . . . . | $\left(\left.\begin{matrix}C^2H^4(C^2H^5O)\\C^2H^4(C^2H^5O)\end{matrix}\right\}O\right)$ |
| Chloroxymethylic ether . . . | $\left(\left.\begin{matrix}C^2H^4(CH^3O)\\C^2H^3Cl\end{matrix}\right\}O\right)$ |

Dioxymethylic ether has not yet been obtained.

The formulæ which M. Lieben has given to these bodies, and which we have here reproduced, are only considered as provisional by this chemist. He employs them until more complete examination shall have determined the real constitution of these compounds. Unpublished and as yet imperfect experiments, which he has been good enough to communicate to me, tend to make me believe that the substitution of $Cl^2$ for $H^2$ in the ether is made at the cost of a single molecule of ethyl. If it be really so, the compounds of which we have just spoken ought to have the following formulæ:

$$\left(\left.\begin{matrix}C^2H^3Cl^2\\ C^2H^5\end{matrix}\right\}O\right)$$

Monochlorinated ether.

$$\left(\left.\begin{matrix}C^2H^3Cl(C^2H^5)\\ C^2H^5\end{matrix}\right\}O\right)$$

Chlorethylic ether.

$$\left(\left.\begin{matrix}C^2H^3Cl(CH^3)\\ C^2H^5\end{matrix}\right\}O\right)$$

Chloromethylic ether.

$$\left(\left.\begin{matrix}C^2H^3(C^2H^5)^2\\ C^2H^5\end{matrix}\right\}O\right)$$

Diethylic ether.

$$\left(\left.\begin{matrix}C^2H^3(CH^3)^2\\ C^2H^5\end{matrix}\right\}O\right)$$

Dimethylic ether.

$$\left(\left.\begin{matrix}C^2H^3Cl(C^2H^5O)\\ C^2H^5\end{matrix}\right\}O\right)$$

Chloroxethylic ether.

$$\left(\left.\begin{matrix}C^2H^3(C^2H^5O)^2\\ C^2H^5\end{matrix}\right\}O\right)$$

Dioxethylic ether.

$$\left(\left.\begin{matrix}C^2H^3Cl(CH^3O)\\ C^2H^5\end{matrix}\right\}O\right)$$

Chloroxymethylic ether.

PROOFS IN SUPPORT OF THE ACTUAL FORMULA OF ETHER.—Before adopting an atomic weight equal to 16 for oxygen and to 12 for carbon, our formula of alcohol ($C^2H^6O$) was ($C^4H^6O^2$), and that of ether, which now is ($C^4H^{10}O$), was ($C^8H^{10}O^2$). But this latter was divisible by 2, and might be written ($C^4H^5O$). Moreover, as water was (HO), the formula ($C^4H^5O$) appeared more simple for ether, because it was thus derived from alcohol by simple dehydration.

$$\underset{\text{Alcohol.}}{(C^4H^6O^2)} = \underset{\text{Ether.}}{(C^4H^5O)} + \underset{\text{Water.}}{(HO)}$$

The adoption of the new atomic weights obliged this formula of ether to be doubled, because oxygen cannot enter into a compound except in atomic proportions; hence the great differences between those chemists who double this formula according to the new theory and those who, faithful to the old ideas, refuse to double it.

The necessity for doubling the formula of ether, even with the old notation, is of such importance that we will detail the reasons which have induced chemists to adopt this course. It is one of the facts which have greatly contributed to the establishment of our present ideas.

1st. To bring ether to the same gaseous volume as the other bodies its formula must be doubled.

2nd. The theory of etherification, demonstrated by Mr. Williamson, proves that two molecules of alcohol always intervene to form ether, and that sulphuric acid does not act as a mere dehydrant, as was believed.

3rd. In the preparation of ether by means of the simple ethers and a sodium derivative of an alcohol, it will again be seen that in order to form the ether it is necessary that two molecules of alcohol should enter into the reaction.

4th. There exist mixed ethers which contain radicles of two different alcohols, and these bodies are formed by reactions which are identical with those which produce ethers proper.

5th. M. Lieben has obtained ethylic ether ($C^4H^{10}O$), in which one atom of hydrogen is replaced by chlorine and another by ethyl; the hydrogen in the ether can therefore be replaced by tenth parts, which fully proves that the molecule of this body contains at least ten atoms of that element.

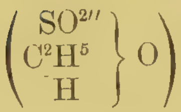
**Nomenclature of the Ethers.**—The ethers properly so called are also named oxides of the alcoholic radicle. Thus we may say oxide of amyl, or amylic ether.

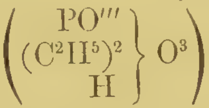
Mixed ethers are named by adding to this generic word the names of the two alcohols which enter into their composition united into a single word. They are also called oxides of the two radicles they contain. Thus the compound $\left(\left.\begin{matrix}C^2H^5\\C^5H^{11}\end{matrix}\right\} O\right)$ is called indiscriminately mixed ethylamylic ether, or oxide of ethyl and amyl.

The simple ethers are called hydrochloric, hydrobromic, hydriodic, hydrofluoric, hydrocyanic ethers; their name being thus preceded by a word which indicates from what alcohol the ether is derived. They are also designated as chlorides, bromides, iodides, fluorides, cyanides of the alcohol radicles. The compound $\left(\left.\begin{matrix}C^7H^{15}\\Cl\end{matrix}\right\}\right)$ is both "heptyl-hydrochloric ether" and "chloride of heptyl."

In naming the compound ethers, the word ether follows the name of the acid of which the body contains the elements, and that of the acid is preceded by a word which indicates the alcohol from which it has been prepared. They may also be named like metallic salts, taking for specific name that of their alcohol radicle. The words ethyl-acetic ether, and acetate of ethyl, both indicate the compound $\left(\left.\begin{matrix}C^2H^3O\\C^2H^5\end{matrix}\right\} O\right)$.

The neutral compound ethers formed by polybasic acids are named in the same way as the preceding; the acid ethers are designated by preceding the word acid by a compound name formed by the name of the acid whose elements enter into their constitution, to which is prefixed the name of the radicle of the alcohol. That part of the word which designates the radicle is preceded by the syllables di, tri, etc., to designate the number of atoms of these radicles.

The compound  $\left(\left.\begin{array}{c}SO^{2''}\\C^2H^5\\H\end{array}\right\} O\right)$ is thus named ethylsulphuric acid. (It is also called sulphovinic acid.)

The compound  $\left(\left.\begin{array}{c}PO'''\\(C^2H^5)^2\\H\end{array}\right\} O^3\right)$ is called diethylphosphoric acid.

When several different radicles enter into an ether, they should be indicated; thus: ethyl-amyl-phosphoric acid, or phosphate of methyl, ethyl, amyl, etc.

**Primary Monatomic Alcohols really known.**—The primary monatomic alcohols which are actually known are the following:

SATURATED ALCOHOLS.—1st. *Alcohols of the series* $C^nH^{2n+2}O$.

Methylic alcohol, or hydrate of methyl:

$$\left(CH^4O\right) = \left(\left.\begin{array}{c}CH^3\\H\end{array}\right\} O\right)$$

Ethylic or ordinary alcohol, or hydrate of ethyl:

$$\left(C^2H^6O\right) = \left(\left.\begin{array}{c}C^2H^5\\H\end{array}\right\} O\right)$$

Propylic alcohol, or hydrate of propyl:

$$\left(C^3H^8O\right) = \left(\left.\begin{array}{c}C^3H^7\\H\end{array}\right\} O\right)$$

Butylic alcohol, or hydrate of butyl:

$$\left(C^4H^{10}O\right) = \left(\left.\begin{array}{c}C^4H^9\\H\end{array}\right\} O\right)$$

Amylic alcohol, or hydrate of amyl:

$$\left(C^5H^{12}O\right) = \left(\left.\begin{array}{c}C^5H^{11}\\H\end{array}\right\} O\right)$$

Caproic or hexylic alcohol, or hydrate of hexyl:

$$\left(C^6H^{14}O\right) = \left(\left.\begin{array}{c}C^6H^{13}\\H\end{array}\right\} O\right)$$

Œnanthylic or heptylic alcohol, or hydrate of heptyl:

$$\left(C^7H^{16}O\right) = \left(\left.\begin{array}{c}C^7H^{15}\\H\end{array}\right\} O\right)$$

Caprylic or octylic alcohol, or hydrate of octyl:

$$\left(C^8H^{18}O\right) = \left(\left.\begin{array}{c}C^8H^{17}\\H\end{array}\right\} O\right)$$

Cetylic or ethal alcohol, or hydrate of cetyl:

$$\left(C^{16}H^{34}O\right) = \left(\left.\begin{array}{c}C^{16}H^{33}\\H\end{array}\right\} O\right)$$

Cerylic alcohol, or hydrate of ceryl:

$$\left(C^{27}H^{56}O\right) = \left(\left.\begin{matrix}C^{27}H^{55}\\H\end{matrix}\right\}O\right)$$

Myricic alcohol, or hydrate of myricyl:

$$\left(C^{30}H^{62}O\right) = \left(\left.\begin{matrix}C^{30}H^{61}\\H\end{matrix}\right\}O\right)$$

2nd. *Alcohols of the series* $C^nH^{2n-6}O$.

Benzylic alcohol, or hydrate of benzyl:

$$\left(C^{7}H^{8}O\right) = \left(\left.\begin{matrix}C^{7}H^{7}\\H\end{matrix}\right\}O\right)$$

Toluic alcohol, or hydrate of toluyl:

$$\left(C^{8}H^{10}O\right) = \left(\left.\begin{matrix}C^{8}H^{9}\\H\end{matrix}\right\}O\right)$$

Cuminic alcohol, or hydrate of cumyl:

$$\left(C^{10}H^{14}O\right) = \left(\left.\begin{matrix}C^{10}H^{13}\\H\end{matrix}\right\}O\right)$$

Sycocerylic alcohol, or hydrate of sycoceryl:

$$\left(C^{18}H^{30}O\right) = \left(\left.\begin{matrix}C^{18}H^{29}\\H\end{matrix}\right\}O\right)$$

NON-SATURATED ALCOHOLS.—1st. *Alcohols of the series* $C^nH^{2n}O$.

Acetylenic alcohol:

$$\left(C^{2}H^{4}O\right) = \left(\left.\begin{matrix}C^{2}H^{3}\\H\end{matrix}\right\}O\right)$$

Allylic alcohol:

$$\left(C^{3}H^{6}O\right) = \left(\left.\begin{matrix}C^{3}H^{5}\\H\end{matrix}\right\}O\right)$$

2nd. *Alcohols of the series* $C^nH^{2n-2}O$.

Campholic alcohol, or Borneo camphor:

$$\left(C^{10}H^{18}O\right) = \left(\left.\begin{matrix}C^{10}H^{17}\\H\end{matrix}\right\}O\right)$$

3rd. *Alcohols of the series* $C^nH^{2n-8}O$.

Cinnamic alcohol:

$$\left(C^{9}H^{10}O\right) = \left(\left.\begin{matrix}C^{9}H^{9}\\H\end{matrix}\right\}O\right)$$

Cholesteric alcohol:

$$\left(C^{26}H^{44}O\right) = \left(\left.\begin{matrix}C^{26}H^{43}\\H\end{matrix}\right\}O\right)$$

### THE MOST IMPORTANT PRIMARY MONATOMIC ALCOHOLS.

**Methylic Alcohol** $\left(C\left\{\begin{matrix}H^3\\OH\end{matrix}\right.\right)$. — *Preparation.*— Methylic alcohol, or wood-spirit, is found among the products of the dry distillation of wood, where it exists mixed with acetic acid, water, and a number of other substances.

In order to extract it from the mixture, the latter is distilled, care being taken that the operation be arrested when the tenth part of the liquid has passed over, and the product is rectified over quicklime.

The liquid thus obtained is mixed with chloride of calcium and distilled in a water-bath. The impurities distil, while the wood-spirit remains combined with the chloride of calcium. If the residue be then heated with water, this combination is destroyed and methylic alcohol distils over. It is separated from the water it still contains by a second rectification from quicklime.

The methylic alcohol which has undergone these different operations is still not perfectly pure. In order to purify it entirely, it must be distilled with a mixture of sulphuric and oxalic acids, which transforms it into oxalate of methyl. This oxalate is solid and may be easily obtained in a pure state by crystallization. Finally, it is saponified by means of an alkaline solution, and the product dehydrated by distilling a third time from quicklime.

*Properties.*—Methylic alcohol is liquid and colourless, is without action on test paper, and has a density of 0·8142 at 0°. It can be mixed with water in all proportions and the mixture does not become turbid. It does not give any black precipitate with mercurous nitrate. It boils at 66°·5, burns with a dull-blue flame, and has an empyreumatic odour.

Wood-spirit mixes with alcohol, ether, essences, and oils. It dissolves phosphorus and sulphur sparingly. It combines with baryta, dissolving it, and also dissolves potash; but these latter solutions become brown and rapidly alter when exposed to the air.

When wood-spirit is dropped on to platinum black, the access of air being regulated, it oxidizes, and is transformed into formic acid:

$$\underset{\text{Wood-spirit.}}{\left(C\left\{\begin{matrix}H^3\\OH\end{matrix}\right.\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} = \underset{\text{Formic acid.}}{\left(C\left\{\begin{matrix}H\\O\\OH\end{matrix}\right.\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}.$$

But, whatever oxidizing methods may be used, formic aldehyd $\left(C\left\{\begin{matrix}H\\O\\H\end{matrix}\right.\right)$ is never procured. This body appears to be too instable to be obtained.

When the vapour of methylic alcohol is transmitted over strongly-heated potash-lime, hydrogen is disengaged, and formiate of potassium is formed. But, as on contact with alkalies in excess, the formiates are transformed into oxalates, hydrogen being disengaged, oxalate of potassium is almost always obtained in this reaction :

$$\underset{\text{Methylic alcohol.}}{\left(C\left\{\begin{matrix}H^3\\OH\end{matrix}\right.\right)} + \underset{\text{Hydrate of potassium.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Formiate of potassium.}}{\left(C\left\{\begin{matrix}H\\O\\OK\end{matrix}\right.\right)} + \underset{\text{Hydrogen.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}\right)}$$

With wood-spirit, chlorine gives compounds which are imperfectly known. Chloride of lime transforms it into chloroform. Bromine or iodine, added to a solution of potash in wood-spirit, give bromoform or iodoform. When heated with chloride of ammonium, methylic alcohol is converted into the chlorides of methyl-, of dimethyl-, and of trimethyl-ammonium.

Sulphuric acid mixed with wood-spirit evolves heat, and gives rise to the formation of methyl-sulphuric acid, which crystallizes on the spontaneous evaporation of the liquid.

$$\underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Wood-spirit.}}{\left(\left.\begin{matrix}CH^3\\H\end{matrix}\right\}O\right)} = \underset{\text{Methyl-sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2''}\\CH^3\\H\end{matrix}\right\}O^2\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

When a mixture of wood-spirit and sulphuric acid is heated, a gaseous product, the oxide of methyl $\left(\left.\begin{matrix}CH^3\\CH^3\end{matrix}\right\}O\right)$, is obtained. But in no case is methylene $(CH^2)$ formed. This latter body does not appear to be stable in the free state.

The hydracids easily transform wood-spirit into simple ethers. Chloride of methyl is gaseous and does not liquify at −18°. Water dissolves 2·8 times its volume at 16°; its density is 1·736; the iodide is liquid and boils at 42°·2 under a pressure of $752^{mm}$.

The oxychloride of carbon becomes greatly heated when mixed with wood-spirit, and transforms this body into chlorocarbonate of methyl.

$$\underset{\text{Wood-spirit.}}{\left(\left.\begin{matrix}CH^3\\H\end{matrix}\right\}O\right)} + \underset{\text{Chloride of carbonyl.}}{\left(CO''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)} = \underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Chlorocarbonate of methyl.}}{\left(CO''\left\{\begin{matrix}OCH^3\\Cl\end{matrix}\right.\right)}$$

Sodium dissolves in methylic alcohol, disengaging hydrogen. In this case methylate of sodium is produced :

$$\underset{\text{Methylic alcohol.}}{2\left(\left.\begin{matrix}CH^3\\H\end{matrix}\right\}O\right)} + \underset{\text{Sodium.}}{\left.\begin{matrix}Na\\Na\end{matrix}\right\}} = \underset{\text{Methylate of sodium.}}{2\left(\left.\begin{matrix}CH^3\\Na\end{matrix}\right\}O\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}}$$

Nevertheless, the quantity of sodium corresponding theoretically to this equation cannot be dissolved. As soon as a small quantity of methylate of sodium is formed, the mass becomes pasty and the sodium ceases to dissolve. The solution may indeed be facilitated by applying heat, but then the methylate of sodium partially decomposes, and its colour becomes brown.

### *Appendix to Wood-spirit.—Chloroform, Bromoform, and Iodoform.*

**Chloroform** ($CHCl^3$).—Chloroform may be considered as trichlorinated marsh gas or bichlorinated chloride of methyl. It may be obtained by causing chlorine to act either on marsh gas or on chloride of methyl. But these methods of preparation are long, costly, and laborious, and have only a theoretical importance, not being practically useful.

Fortunately, chloroform is also produced in a number of other reactions, which, though complicated in a theoretical point of view, are simple in practice. Soubeyran recommends the following process of preparation.

*Preparation.*—Ten kilogrammes of chloride of lime and three of slaked lime, mixed with sixty of water, are placed in a still which must be capacious enough to be only a third full; then two kilogrammes of alcohol at 85° are added, and the whole is quickly heated. The reaction commences about 80°, and takes place so actively that the fire must be removed or the mass will overflow. Distillation then commences and proceeds almost by itself. About three litres of the liquid, which is divided into two layers, are collected: one of these layers consists of water; the other, which is heavier, of chloroform, mixed with alcohol and chlorine.

The lower layer is separated and washed, first with water to remove the alcohol, then with a solution of carbonate of potassium to remove the chlorine. Finally, it is dried by chloride of calcium and distilled. In this operation, the quicker the temperature of 80° is attained the more will there be of the product obtained. Therefore it is better to mix the lime with hot water.

The alcohol may be replaced by wood-spirit or acetone in this preparation; but the chloroform is then adulterated with a chlorinated oil, from which it must be freed by distillation with sulphuric acid.

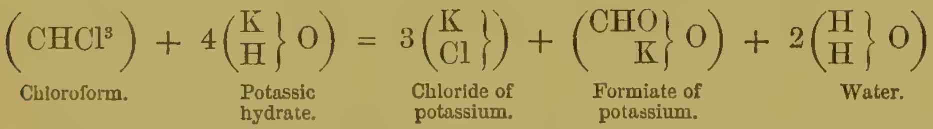
*Properties.*—Chloroform is a colourless and very clear liquid; its taste is first pungent, then fresh and sweet. Its density is 1·491 at 17°. It has a very agreeable ethereal odour. Its boiling point is 61° according to Regnault, and 63°·5 under a pressure of 0·772 according to Pierre; its vapour density has been found to be 4·199 – 4·230.

Chloroform ignites with difficulty; however, when a cotton wick is impregnated with it, it burns with a green flame. If a moistened glass be placed over this flame hydrochloric acid will be condensed, which may be recognized by the precipitate which is produced when an aqueous solution of nitrate of silver is added to it. This latter reaction, and the green colour of the flame, are characteristics of all chlorinated, brominated, or iodized organic substances. With these latter, however, the colour of the flame approaches more to blue. Chloroform is only slightly soluble in water, to which it communicates a very agreeable sweet taste. It is very soluble in alcohol and ether; concentrated sulphuric acid does not dissolve it.

Pure chloroform should fall to the bottom of water without making it cloudy, while when mixed with alcohol it becomes milky. This latter impurity may also be recognized from the circumstance that pure chloroform does not become green with a mixture of sulphuric acid and potassic bichromate, while it assumes this colour if it contains alcohol.

Chloroform dissolves most organic matters which are rich in carbon. It readily dissolves caoutchouc, which it deposits unaltered on evaporation.

When distilled in a current of chlorine, it is converted into hydrochloric acid and perchloride of carbon: heated with an alcoholic solution of potash, chloroform is converted into potassic formiate and chloride:



$$\underset{\text{Chloroform.}}{\left(\mathrm{CHCl^3}\right)} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{4\left(\left.\begin{matrix}\mathrm{K}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\substack{\text{Chloride of}\\\text{potassium.}}}{3\left(\left.\begin{matrix}\mathrm{K}\\\mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\substack{\text{Formiate of}\\\text{potassium.}}}{\left(\left.\begin{matrix}\mathrm{CHO}\\\mathrm{K}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}$$

Chloroform vapour, mixed with air, produces complete anæsthesia when breathed. The anæsthesia is preceded by a period of excitement which only lasts a short time. This anæsthetic property is much used in surgery.

**Bromoform** ($CHBr^3$).—*Preparation.*—This body is obtained by causing potash and bromine to act simultaneously on wood-spirit, alcohol or acetone; it is also obtained by submitting aqueous citric and malic acids to the action of bromine, or by treating bromal ($C^2HBr^3O$) with alkalies.

The first process is the most simple. One part of potash is dissolved in one part of wood-spirit, and sufficient bromine is added to slightly colour the liquid. A layer of bromoform is deposited at the bottom of the liquid; it is washed, dried over chloride of calcium, and distilled.

*Properties.*—Bromoform is a clear liquid; its density is 2·13; it possesses an agreeable odour and a sweet taste. Its boiling point has not been determined with certainty, but it is less volatile than chloroform. It is very slightly soluble in water, to which it nevertheless communicates its odour and taste. Alcohol, ether, and essential oils, on the contrary, dissolve it with ease.

It behaves in the same manner as chloroform with re-agents; but splits up more readily than this latter into bromide and formiate under the influence of alkalies.

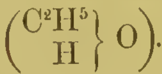
**Iodoform** ($CHI^3$). — *Preparation.* — M. Filhol recommends the following method of preparing this body to be employed:

Two parts of crystallized carbonate of sodium are dissolved in ten parts of water, and one part of alcohol is added. The liquid is then heated to 60° or 80° and one part of iodine is thrown in gradually. At the end of the operation, the iodoform is deposited at the bottom of the hot liquid, which is filtered to separate the deposit; two fresh parts of carbonate of sodium are introduced into the mother-liquor, which is kept at 60° or 80°, and an additional part of alcohol is added. A current of chlorine is then transmitted rapidly through the liquid, a large quantity of nascent iodine is thus constantly in contact with the alcohol, and iodoform is produced in abundance. When a considerable quantity of the product has been formed, the action of the chlorine is arrested, the liquid is filtered, and, if necessary, the mother-liquor may be treated as before, and a third proportion of iodoform obtained.

Iodoform crystallizes in small pearly scales of a yellow colour, very friable and greasy to the touch. Its odour resembles that of saffron; its density is about 2·0; it does not perceptibly dissolve in water, but it is very soluble in alcohol, ether, oils, and essences. It melts between 115° and 120°; part vaporizes without alteration, and part is decomposed. It may be distilled with the vapour of water.

Under the influence of the alkalies, iodoform is converted into an alkaline formiate and iodide.

Iodoform is a local anæsthetic, and is used as such in medicine.



**Ethylic or Ordinary Alcohol** $\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)$.—*Preparation.*—When ordinary sugar, dissolved in water, is left in presence of organic matter, and a little beer yeast is added to the liquid, fermentation is produced, the first effect of which is to split up the cane-sugar, when that is used, into glucose and levulose; and it then transforms these latter bodies into carbonic anhydride, alcohol, propylic alcohol, butylic alcohol, amylic alcohol, glycerine, succinic acid, etc. This transformation results from a vital action. M. Pasteur has clearly shown that the microscopic cells of which yeast is composed are true mycoderms, which live at the expense of the fermenting substances, and transform them into a number of different products. The transformation of sugar into alcohol cannot therefore be represented by any chemical equation: as all those by which it could be represented would be too simple and erroneous.

Generally, alcohol is extracted from wine (fermented grape-juice) or from the product of the fermentation of the juice of beet-root, or, again, from the product of the fermentation of glucose obtained by the saccharification of starch, rice, or other cereals of inferior quality.

In order to extract it from these substances they are submitted to distillation. Alcohol being more volatile than water, first passes over, and if, as in manufactories, the apparatus is so contrived that the least volatile portions constantly fall again into the still, two distillations are sufficient to produce alcohol containing only two per cent. of water.

These two parts of water cannot however be removed by distillation. To do this, quicklime which is covered with alcohol of 98 p. c. is placed in a retort. The cover is then put on this retort, all its openings are closed, and the whole is left for 24 hours. The lime swells during this time and absorbs the water which the alcohol contained. After 24 hours it is distilled, and if the product be not perfectly anhydrous, it must be left for 24 hours in contact with anhydrous baryta in a well-stoppered glass globe, and then again distilled.

Alcohol may also be obtained by the different general processes we have described; but though these are so interesting in a theoretical point of view, they cannot be used practically.

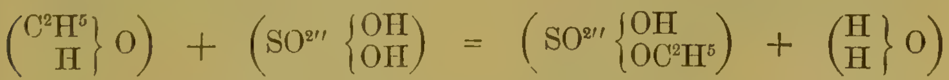
In order to ascertain whether the alcohol be quite anhydrous, it is placed in contact with sulphate of copper which has been deprived of its water of crystallization by heat, and is consequently perfectly white. If the alcohol contain water the sulphate of copper assumes a blue tint.

*Properties.*—When pure, alcohol is a colourless and very volatile liquid of an agreeable odour; its density is 0·792 at 20°. It has an acrid burning taste, which loses much of its intensity when diluted with water; it boils at 78°·4 under a pressure of $760^{mm}$; it is not solidified by a cold of $-100°$, but it becomes viscid at that temperature. Its vapour density is 1·6133. It is very inflammable, and burns with a dull-blue flame.

Alcohol mixes with water in every proportion. The mixture is accompanied by disengagement of heat and a contraction, which reaches the maximum when 116 parts of water are added to 100 parts of alcohol.

Alcohol dissolves resins, ethers, essential oils, alkaloids, many of the organic acids, bromine, iodine, sulphur and phosphorus slightly, and certain mineral salts, such as the perchloride of mercury and nitrate of uranium.

Sulphuric acid becomes considerably heated when mixed with alcohol. When such a mixture is made, care must always be taken to pour the sulphuric acid into the alcohol, shaking it continually, and not the alcohol into the sulphuric acid. Sulphovinic acid and water are produced in this reaction.

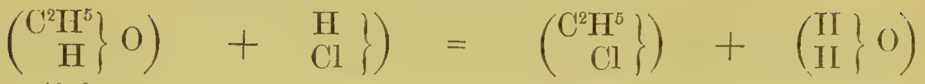


$$\underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)} + \underset{\text{Sulphuric acid.}}{\left(SO^{2''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)} = \underset{\text{Sulphovinic acid.}}{\left(SO^{2''}\left\{\begin{matrix}OH\\OC^2H^5\end{matrix}\right.\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

If water be added to the mixture, and it be then saturated with carbonate of barium, barytic sulphate which precipitates is formed, while sulphovinate of the same metal remains in solution. The liquid is then filtered, and when left to spontaneous evaporation it deposits this salt in beautiful crystals.

If, on the contrary, the mixture of sulphuric acid and alcohol be heated, ether is formed which distils if the proportion of sulphuric acid be not too great; and ethylene if the contrary be the case. (*See* Ethers proper, p. 417.)

The hydracids passed in a gaseous state through alcohol, transform it into chloride, bromide, iodide, or fluoride of ethyl:



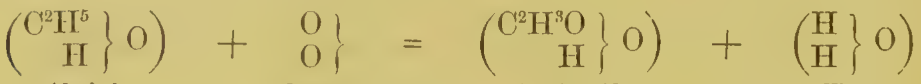
$$\underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\ H\end{matrix}\right\}O\right)} + \underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\ Cl\end{matrix}\right\}\right)} = \underset{\text{Chloride of ethyl.}}{\left(\left.\begin{matrix}C^2H^5\\ Cl\end{matrix}\right\}\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)}$$

Mineral or organic oxyacids also unite with alcohol, eliminating water and giving rise to compound ethers. When they are strong, the action takes place in the cold, as with sulphuric acid. When, on the contrary, they are weak like acetic acid, their mixture with alcohol must be heated to 200° in hermetically-sealed tubes, or this mixture must be submitted to a current of hydrochloric acid. (*See* Compound Ethers, p. 415.)

Mercuric nitrate does not attack alcohol, but when mercury is dissolved in nitric acid in presence of alcohol, a fulminating product is obtained—the fulminate of mercury—which is used in the manufacture of gun-caps.

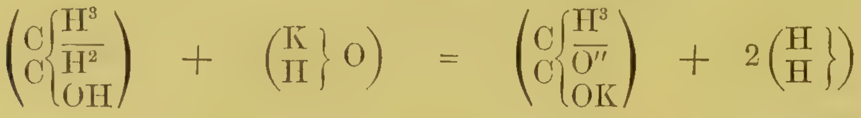
Chromic acid oxidizes alcohol so actively that the liquid takes fire.

On contact with platinum black, alcohol is transformed into acetic acid:



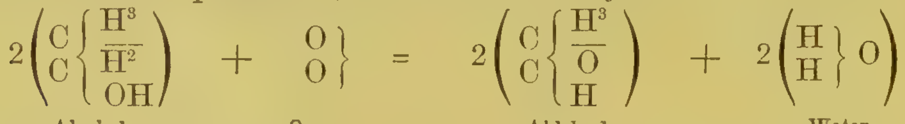
$$\underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\ H\end{matrix}\right\}O\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\ O\end{matrix}\right\}} = \underset{\text{Acetic acid.}}{\left(\left.\begin{matrix}C^2H^3O\\ H\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)}$$

It gives acetate of potassium with disengagement of hydrogen, when its vapours are transmitted over strongly-heated potash-lime:



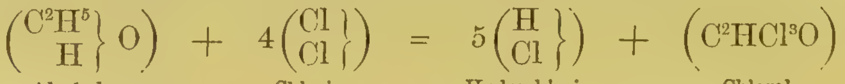
$$\underset{\text{Alcohol.}}{\left(\begin{matrix}C\\ C\end{matrix}\left\{\begin{array}{l}\underline{H^3}\\ H^2\\ OH\end{array}\right.\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\ H\end{matrix}\right\}O\right)} = \underset{\text{Acetate of potassium.}}{\left(\begin{matrix}C\\ C\end{matrix}\left\{\begin{array}{l}\underline{H^3}\\ O''\\ OK\end{array}\right.\right)} + 2\underset{\text{Hydrogen.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}\right)}$$

Heated with a mixture of sulphuric acid and binoxide of manganese or bichromate of potassium, it furnishes aldehyd:



$$2\underset{\text{Alcohol.}}{\left(\begin{matrix}C\\ C\end{matrix}\left\{\begin{array}{l}\underline{H^3}\\ H^2\\ OH\end{array}\right.\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\ O\end{matrix}\right\}} = 2\underset{\text{Aldehyd.}}{\left(\begin{matrix}C\\ C\end{matrix}\left\{\begin{array}{l}\underline{H^3}\\ O\\ H\end{array}\right.\right)} + 2\underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)}$$

Chlorine attacks alcohol strongly when this liquid is perfectly anhydrous: hydrochloric acid and chloral are formed.



$$\underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\ H\end{matrix}\right\}O\right)} + 4\underset{\text{Chlorine.}}{\left(\left.\begin{matrix}Cl\\ Cl\end{matrix}\right\}\right)} = 5\underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\ Cl\end{matrix}\right\}\right)} + \underset{\text{Chloral.}}{\left(C^2HCl^3O\right)}$$

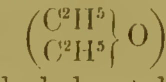
Many neutral salts, such as iodide of mercury, chloride of ammonium and others, etherify alcohol when they are heated to between 200° and 300° with this liquid in hermetically-sealed tubes. In the case of chloride of ammonium there are formed, in addition to ether, the chlorides of ethyl-ammonium, biethyl-ammonium, and triethyl-ammonium.

Estimation of Alcohol.—Spirits, wines, liqueurs, and spirituous liquids in general are usually valued according to the quantity of pure alcohol they contain. The method employed to determine this proportion is based on the difference of density according to the amount of water with which it is mixed. Gay-Lussac constructed an hydrometer so graduated that, when plunged into such a mixture, it at once indicates the per centage. But as the indications of this instrument vary with the temperature, and as it has been graduated for a temperature of 15°, when the operation is conducted at a higher or lower temperature the indications of the hydrometer must be corrected accordingly. This is done by the assistance of a table of corrections calculated by Gay-Lussac. Moreover, this correction may be calculated without the table by means of the formula $x = c \pm 0{\cdot}4t$, in which $x$ expresses the quantity of the alcohol contained in the liquid, $c$ the degree observed in Gay-Lussac's hydrometer, and $t$ the number of degrees which separates the temperature observed from 15°; the second figure is subtracted from the first when the temperature is higher than 15°, and added if the contrary be the case.

If the liquid whose quantity of alcohol has to be determined does not contain alcohol and water exclusively, if, for instance, it holds solid substances in solution which may have an influence on its density, the preceding process cannot be directly applied. In order to employ it, the liquid must first be submitted to distillation, in order to eliminate the foreign substances. The fourth part of the liquid is generally collected in the distillation, and there is added to this distilled part a quantity of pure water sufficient to restore its volume to that of the original liquid. The hydrometer is then used as we have just explained. The distilled liquid need not have the water added to it, the degree might be taken immediately; but then, in order to bring the degree observed to that of the liquid in question, it must be divided by four, if the fourth part have been exactly collected; by three if it were the third part, and so on.

A useful apparatus is sold in commerce for the purpose of these operations. It consists of a small flask, the neck of which is closed by an india-rubber stopper having a tube adapted which unites the flask to a small refrigerator. Fig. 49 (page 432) shows the apparatus and the mode of using it.

### *Appendix to Ethylic Alcohol.*

**Oxide of Ethyl** (*Ether*)  $\left(\begin{matrix} C^2H^5 \\ C^2H^5 \end{matrix}\right\} O \Bigg)$.—*Preparation.*—In order to obtain ether from ordinary alcohol, a tubulated retort is half filled with a mixture of 5 parts of alcohol of 90 per cent., and 9 parts of concentrated sulphuric acid. This retort is placed in communication with a condensing apparatus, while the upper tubulure communicates, by means of a tube with a stopcock, with a large vessel full of alcohol (fig. 50). The retort being heated in a sand-bath, ether begins to distil over. Then, from time to time, a quantity of alcohol, approximately equal to that which distils in the state of ether, is added to the hot mixture; the operation may be thus continued until, owing to secondary reactions, the liquid of the retort shall have lost its powers of etherification, which does not occur until the operation has been carried on for a considerable time.

E. DS
OOL OF
DICINE

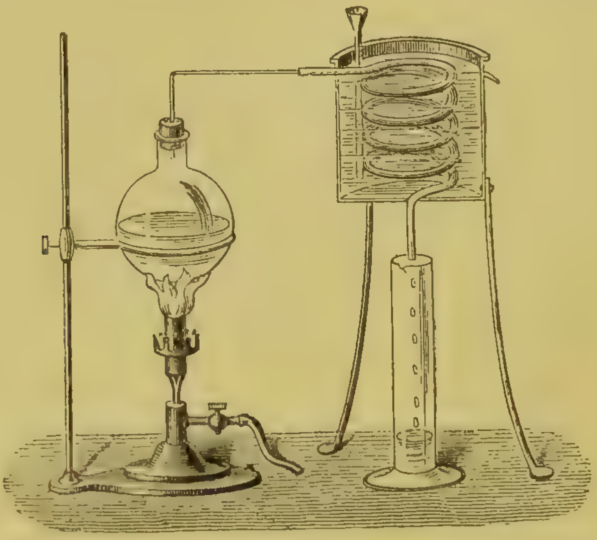


Fig. 49.

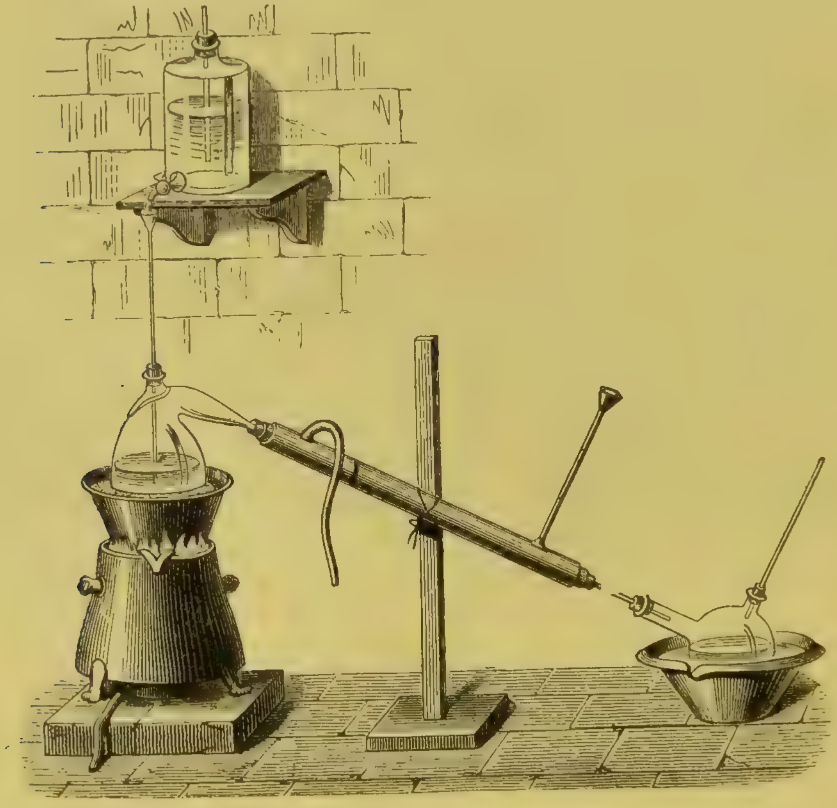


Fig. 50.

We have already seen the theory of this reaction, when speaking of ethers in general.

Ether thus obtained is not pure; it is mixed with water and alcohol, and must be purified by agitating it with water which dissolves it only very sparingly, but which seizes the alcohol. The ether is then dried over chloride of calcium, and finally distilled. The best method of obtaining it perfectly anhydrous is to leave it for some length of time in contact with pieces of sodium.

*Properties.*—Pure ether is a colourless, limpid, and very volatile liquid; its taste is at first fiery, but afterwards cooling, and it has an agreeable odour. Its density in a liquid state is 0·723, and its vapour density is 2·586. It has a high refracting power, boils at 35°·6, and is solidified at −31° in brilliant laminæ. Ether mixes with alcohol in all proportions, but it is only soluble in 9 times its volume of water; it readily dissolves the essential oils, resins, hydrocarbons, and fatty bodies, and in general substances which are highly carbonized. It dissolves sulphur and phosphorus sparingly, and, among mineral salts, mercuric chloride and uranic nitrate.

Ether is very inflammable; its vapour, mixed with the air, forms an explosive mixture; from its great volatility, it is always dangerous to decant it near a flame.

Sulphuric acid dissolves ether, and the mixture becoming heated is transformed into ethyl-sulphuric acid:

$$\underset{\text{Sulphuric acid.}}{2\left(SO^{2''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)} + \underset{\text{Ether.}}{\left(\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}O\right)} = \underset{\substack{\text{Ethyl-sulphuric}\\\text{(sulphovinic) acid.}}}{2\left(SO^{2''}\left\{\begin{matrix}OH\\OC^2H^5\end{matrix}\right.\right)} + \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O}$$

We will not say more here on the other chemical properties of ether, which have been sufficiently treated of under the head of ethers proper and primary monatomic alcohols in general (p. 417).

Ether, like chloroform, is an anæsthetic, and was formerly used as such, but as owing to its great volatility it is more difficult to administer, and as, besides, it requires a longer time than chloroform to cause anæsthesia, its employment has been superseded by this latter body. It is taken medicinally as an antispasmodic, either mixed with water or in small gelatine capsules.

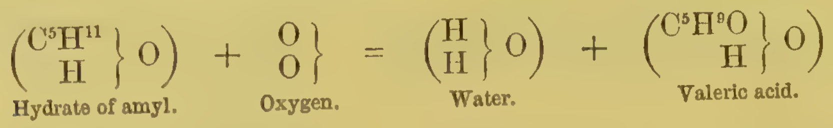
**Amylic Alcohol** $\left(\left.\begin{matrix}C^5H^{11}\\H\end{matrix}\right\}O\right)$.—*Preparation.*—In the manufacture of ordinary alcohol, when the whole, or at least the greater part of the alcohol contained in the fermented liquid has distilled, a residue is left which boils at a higher temperature, and which contains propylic, butylic, and amylic alcohols. The latter is the most abundant of the three. When this residue is submitted to fractional distillation, and that which passes at from 128° to 132° is collected, pure amylic alcohol is obtained.

*Properties.*—The hydrate of amyl is an oily, colourless, and very mobile liquid, of a peculiar odour, and having an acrid, burning taste. When its vapours are inhaled, they produce oppression at the chest, followed by cough. Its density is 0·8111, and its vapour density 3·147. It stains paper, but the stain does not last long; it does not perceptibly dissolve in water, but floats on the top like oil; it readily dissolves in alcohol, in ether, and the different essences; when cooled to − 22° it congeals in crystalline plates.

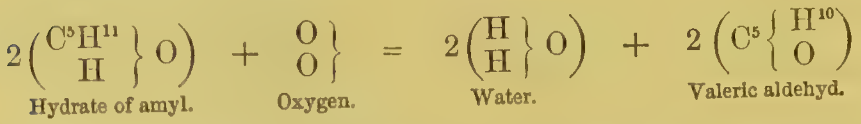
Amylic alcohol generally exercises an action on polarized light, but that prepared artificially by the different processes formerly mentioned is inactive. M. Pasteur has discovered that active amylic alcohol is sometimes dextrogyrate and sometimes levogyrate. That extracted from fermented liquors is a mixture of these two varieties. Therefore, instead of having a constant boiling point, it varies between 128° and 132°; the two varieties having different boiling points, which are very near each other.

When the vapours of amylic alcohol are transmitted through a red-hot tube, they furnish ethylene, propylene, butylene, and amylene.

Amylic alcohol burns readily, with a blue flame. In presence of platinum black it is converted into valeric acid. When heated with a mixture of sulphuric acid and bichromate of potassium, it forms valeric aldehyd.

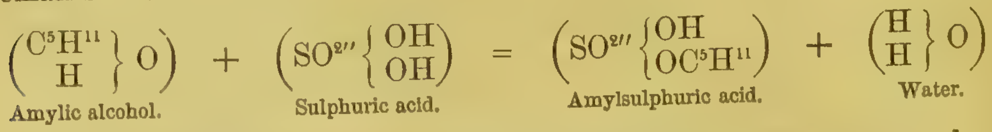


$$\underset{\text{Hydrate of amyl.}}{\left(\left.\begin{matrix}C^5H^{11}\\ H\end{matrix}\right\}O\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\ O\end{matrix}\right\}} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)} + \underset{\text{Valeric acid.}}{\left(\left.\begin{matrix}C^5H^9O\\ H\end{matrix}\right\}O\right)}$$



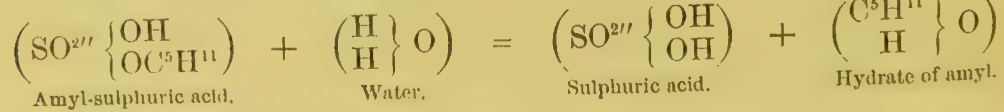
$$\underset{\text{Hydrate of amyl.}}{2\left(\left.\begin{matrix}C^5H^{11}\\ H\end{matrix}\right\}O\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\ O\end{matrix}\right\}} = \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)} + \underset{\text{Valeric aldehyd.}}{2\left(C^5\left\{\begin{matrix}H^{10}\\ O\end{matrix}\right.\right)}$$

Concentrated sulphuric acid readily dissolves amylic alcohol, disengaging heat; if water be added to the mixture, and it be saturated with carbonate of barium, barytic sulphate is precipitated, and sulphamylate of barium, which crystallizes on the evaporation of the liquid, remains in solution:



$$\underset{\text{Amylic alcohol.}}{\left(\left.\begin{matrix}C^5H^{11}\\ H\end{matrix}\right\}O\right)} + \underset{\text{Sulphuric acid.}}{\left(SO^{2''}\left\{\begin{matrix}OH\\ OH\end{matrix}\right.\right)} = \underset{\text{Amylsulphuric acid.}}{\left(SO^{2''}\left\{\begin{matrix}OH\\ OC^5H^{11}\end{matrix}\right.\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)}$$

By submitting this salt to repeated crystallizations, M. Pasteur has been able to separate that arising from the dextrogyrate alcohol from that arising from the levogyrate alcohol, and consequently to obtain these two varieties of the same alcohol in a free state. For this purpose the sulph-amylate of barium is precipitated by sulphuric acid to liberate the amyl-sulphuric acid, and this latter, distilled with water, furnishes amylic alcohol:

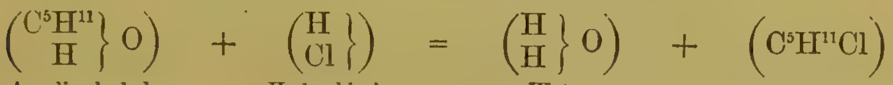


$$\underset{\text{Amyl-sulphuric acid.}}{\left(SO^{2''}\left\{\begin{matrix}OH\\ OC^5H^{11}\end{matrix}\right.\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)} = \underset{\text{Sulphuric acid.}}{\left(SO^{2''}\left\{\begin{matrix}OH\\ OH\end{matrix}\right.\right)} + \underset{\text{Hydrate of amyl.}}{\left(\left.\begin{matrix}C^5H^{11}\\ H\end{matrix}\right\}O\right)}$$

When the solution of hydrate of amyl in concentrated sulphuric acid is distilled, oxide of amyl, amylene, and different hydrocarbides are obtained.

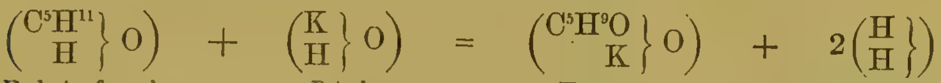
On distilling a solution of chloride of zinc in amylic alcohol, amylene mixed with hydride of amyl is obtained, and also higher homologues of these two bodies.

Under the influence of either oxyacids or hydracids, amylic alcohol is etherified in the same way as the other alcohols:



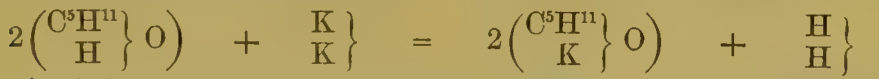
$$\underset{\text{Amylic alcohol.}}{\left(\left.\begin{matrix}C^5H^{11}\\H\end{matrix}\right\}O\right)} + \underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Chloride of amyl.}}{\left(C^5H^{11}Cl\right)}$$

When heated with potash-lime to 220°, hydrate of amyl is converted into valerate of potassium, disengaging hydrogen:



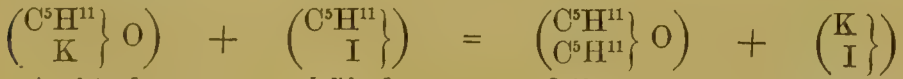
$$\underset{\text{Hydrate of amyl.}}{\left(\left.\begin{matrix}C^5H^{11}\\H\end{matrix}\right\}O\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Valerate of potassium.}}{\left(\left.\begin{matrix}C^5H^9O\\K\end{matrix}\right\}O\right)} + \underset{\text{Hydrogen.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}\right)}$$

Sodium and potassium dissolve in amylic alcohol, producing metallic amylates and disengaging hydrogen.



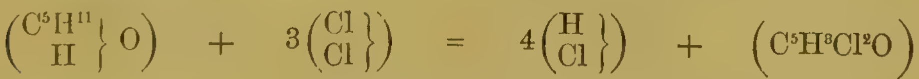
$$\underset{\text{Amylic alcohol.}}{2\left(\left.\begin{matrix}C^5H^{11}\\H\end{matrix}\right\}O\right)} + \underset{\text{Potassium.}}{\left.\begin{matrix}K\\K\end{matrix}\right\}} = \underset{\text{Amylate of potassium.}}{2\left(\left.\begin{matrix}C^5H^{11}\\K\end{matrix}\right\}O\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}}$$

This amylate, when treated by iodide of amyl, furnishes oxide of amyl and iodide of potassium.



$$\underset{\text{Amylate of potassium.}}{\left(\left.\begin{matrix}C^5H^{11}\\K\end{matrix}\right\}O\right)} + \underset{\text{Iodide of amyl.}}{\left(\left.\begin{matrix}C^5H^{11}\\I\end{matrix}\right\}\right)} = \underset{\text{Oxide of amyl.}}{\left(\left.\begin{matrix}C^5H^{11}\\C^5H^{11}\end{matrix}\right\}O\right)} + \underset{\text{Iodide of potassium.}}{\left(\left.\begin{matrix}K\\I\end{matrix}\right\}\right)}$$

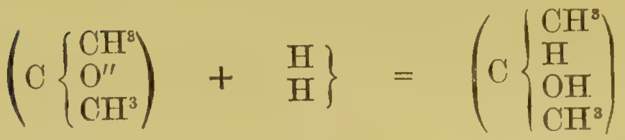
Chlorine acts on hydrate of amyl in the same manner as on all the other alcohols, that is to say, it takes two atoms of hydrogen from it and furnishes products of substitution derived from the alcohol thus dehydrogenized.



$$\underset{\text{Amylic alcohol.}}{\left(\left.\begin{matrix}C^5H^{11}\\H\end{matrix}\right\}O\right)} + \underset{\text{Chlorine.}}{3\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}\right)} = \underset{\text{Hydrochloric acid.}}{4\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Chloramyl.}}{\left(C^5H^8Cl^2O\right)}$$

## SECONDARY MONATOMIC ALCOHOLS.

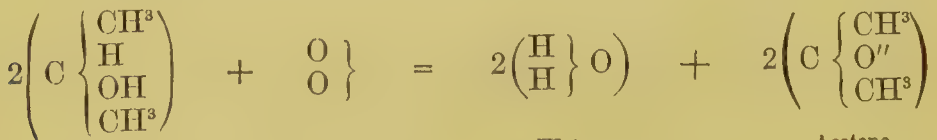
Only one alcohol of this series is yet known, viz., the isopropylic alcohol obtained by M. Friedel by submitting ordinary acetone to the action of nascent hydrogen.



$$\left(C\left\{\begin{matrix}CH^3\\O''\\CH^3\end{matrix}\right.\right) + \left.\begin{matrix}H\\H\end{matrix}\right\} = \left(C\left\{\begin{matrix}CH^3\\H\\OH\\CH^3\end{matrix}\right.\right)$$

Acetone. Hydrogen. Isopropylic alcohol.

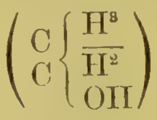
The characteristic property of the secondary alcohols is, that when oxidized they give an acetone which is incapable of being ultimately transformed into an acid, instead of an aldehyd which can be thus transformed. Thus, while propylic alcohol would be converted by oxidation first into propionic aldehyd and then into propionic acid, isopropylic alcohol only furnishes acetone.



$$2\left(C\left\{\begin{matrix}CH^3\\H\\OH\\CH^3\end{matrix}\right.\right) + \left.\begin{matrix}O\\O\end{matrix}\right\} = 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + 2\left(C\left\{\begin{matrix}CH^3\\O''\\CH^3\end{matrix}\right.\right)$$

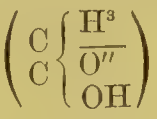
Isopropylic alcohol. Oxygen. Water. Acetone.

This property is thus explained: the transformation of an alcohol into an acid arises from the substitution of O″ for $H^2$:



$$\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\ \hline H^2\\OH\end{matrix}\right.\right)$$

Ethylic alcohol.



$$\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\ \hline O''\\OH\end{matrix}\right.\right)$$

Acetic acid.

in secondary alcohols such a substitution is impossible, as they possess only a single atom of typical hydrogen, the other being replaced by methyl.

Under the influence of bromine, isopropylic alcohol acts like the true alcohols. While these lose $H^2$ under this influence, and are converted into aldehyd, which the bromine afterwards transforms into a product of substitution, it also loses $H^2$, and is converted into acetone, which, by an ulterior action of the bromine, gives ter- and tetra-brominated acetone. The hydrobromic acid liberated in this reaction always reacts on the isopropylic alcohol still undecomposed and gives bromide of isopropyl.

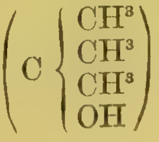
It is probable that all acetones, when treated with nascent hydrogen, would furnish secondary alcohols.

## TERTIARY MONATOMIC ALCOHOLS.

All these alcohols have been obtained by M. Boutlerow; they are four in number, two of them being isomers. They are:

Trimethylated methylic alcohol, or, according to the nomenclature of Messrs. Kolbe and Boutlerow,

Trimethyl-carbinol . . . .



$$\left(C\left\{\begin{matrix}CH^3\\CH^3\\CH^3\\OH\end{matrix}\right.\right) = (C^4H^{10}O)$$

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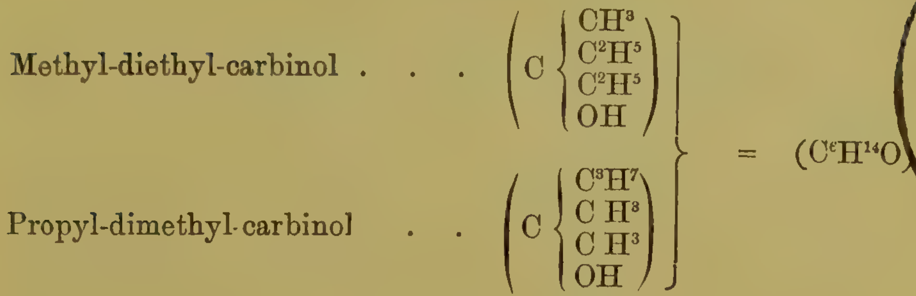
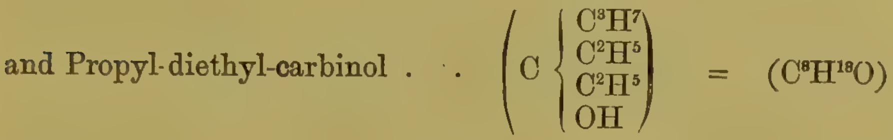


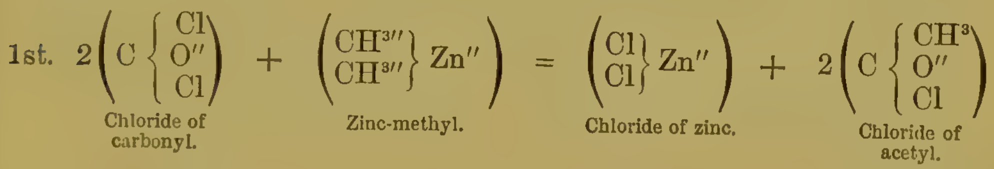
$$\left.\begin{matrix}\text{Methyl-diethyl-carbinol} \quad . \quad . \quad . & \left(C\left\{\begin{matrix}CH^3\\C^2H^5\\C^2H^5\\OH\end{matrix}\right.\right)\\ \text{Propyl-dimethyl-carbinol} \quad . \quad . & \left(C\left\{\begin{matrix}C^3H^7\\C\,H^3\\C\,H^3\\OH\end{matrix}\right.\right)\end{matrix}\right\} = (C^6H^{14}O)$$



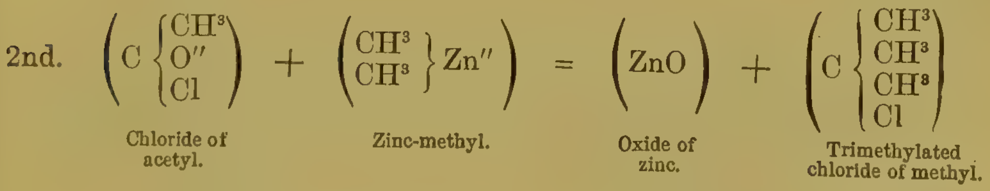
$$\text{and Propyl-diethyl-carbinol} \quad . \quad . \quad \left(C\left\{\begin{matrix}C^3H^7\\C^2H^5\\C^2H^5\\OH\end{matrix}\right.\right) = (C^8H^{18}O)$$

The first of these bodies was obtained by M. Boutlerow, by causing zinc-methyl to act on the chloride of carbonyl or on the chloride of acetyl, and submitting the product thus obtained to the action of water.

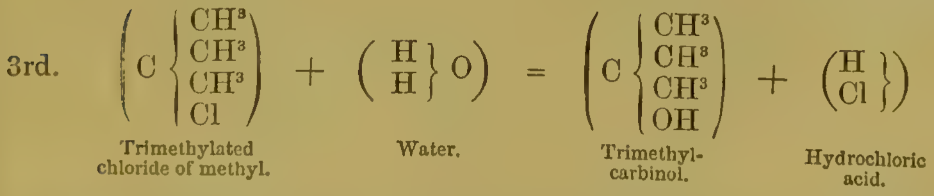
In the case of oxychloride of carbon, the reaction takes place in two stages: in the first, an atom of chlorine is replaced by methyl, and chloride of acetyl is produced; in the second, two atoms of methyl are substituted for the oxygen of the chloride of acetyl and give rise to trimethylated chloride of methyl. This chloride, when treated by water, exchanges its chlorine for (OH) and is thus transformed into trimethyl-carbinol:



$$\text{1st.}\quad \underset{\text{Chloride of carbonyl.}}{2\left(C\left\{\begin{matrix}Cl\\O''\\Cl\end{matrix}\right.\right)} + \underset{\text{Zinc-methyl.}}{\left(\left.\begin{matrix}CH^{3'''}\\CH^{3'''}\end{matrix}\right\}Zn''\right)} = \underset{\text{Chloride of zinc.}}{\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}Zn''\right)} + \underset{\text{Chloride of acetyl.}}{2\left(C\left\{\begin{matrix}CH^3\\O''\\Cl\end{matrix}\right.\right)}$$

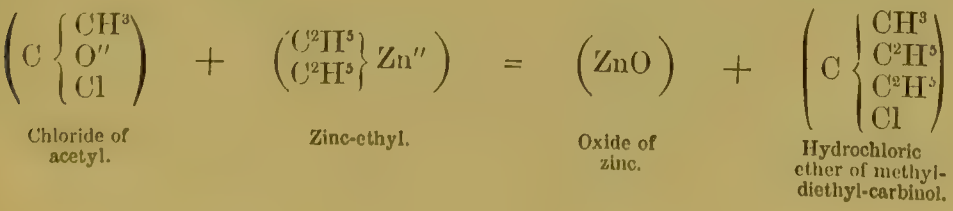


$$\text{2nd.}\quad \underset{\text{Chloride of acetyl.}}{\left(C\left\{\begin{matrix}CH^3\\O''\\Cl\end{matrix}\right.\right)} + \underset{\text{Zinc-methyl.}}{\left(\left.\begin{matrix}CH^3\\CH^3\end{matrix}\right\}Zn''\right)} = \underset{\text{Oxide of zinc.}}{\left(ZnO\right)} + \underset{\text{Trimethylated chloride of methyl.}}{\left(C\left\{\begin{matrix}CH^3\\CH^3\\CH^3\\Cl\end{matrix}\right.\right)}$$



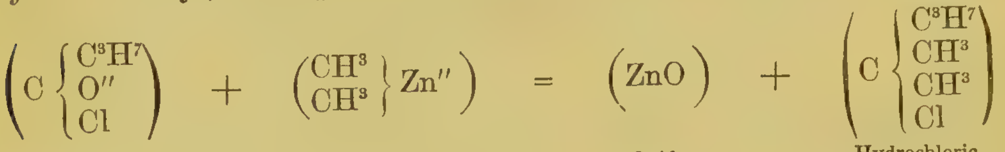
$$\text{3rd.}\quad \underset{\text{Trimethylated chloride of methyl.}}{\left(C\left\{\begin{matrix}CH^3\\CH^3\\CH^3\\Cl\end{matrix}\right.\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Trimethyl-carbinol.}}{\left(C\left\{\begin{matrix}CH^3\\CH^3\\CH^3\\OH\end{matrix}\right.\right)} + \underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)}$$

Methyl-diethyl-carbinol is prepared by causing the chloride of acetyl to react on zinc-ethyl and saponifying by water the chloride obtained:



$$\underset{\text{Chloride of acetyl.}}{\left(C\left\{\begin{matrix}CH^3\\O''\\Cl\end{matrix}\right.\right)} + \underset{\text{Zinc-ethyl.}}{\left(\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}Zn''\right)} = \underset{\text{Oxide of zinc.}}{\left(ZnO\right)} + \underset{\text{Hydrochloric ether of methyl-diethyl-carbinol.}}{\left(C\left\{\begin{matrix}CH^3\\C^2H^5\\C^2H^5\\Cl\end{matrix}\right.\right)}$$

Propyl-dimethyl-carbinol is prepared by treating chloride of butyl by zinc-methyl, and saponifying the product of the reaction by water:



$$\left(C\begin{cases}C^3H^7\\O''\\Cl\end{cases}\right) + \left(\left.\begin{matrix}CH^3\\CH^3\end{matrix}\right\}Zn''\right) = \left(ZnO\right) + \left(C\begin{cases}C^3H^7\\CH^3\\CH^3\\Cl\end{cases}\right)$$

Chloride of butyl. Zinc-methyl. Oxide of zinc. Hydrochloric ether of propyl-dimethyl-carbinol.

Finally, propyl-diethyl-carbinol is prepared by an analogous reaction to the preceding, substituting zinc-ethyl for zinc-methyl.

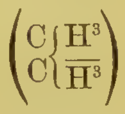
*Properties.*—The properties of tertiary monatomic alcohols have as yet been little studied. It is only known that the action exercised on them by oxidizing agents clearly distinguishes them from the primary and secondary alcohols.

On being oxidized, the primary alcohols give an aldehyd and an acid; the secondary alcohols under the same conditions furnish an acetone. All these derived products contain as many atoms of carbon as the alcohol from which they are derived. The tertiary alcohols, on the contrary, split up on oxidation, and produce bodies, the molecule of which contains less carbon than that of their original alcohol. Thus the trimethyl-carbinol is transformed under the influence of oxidants into a mixture of formic and propionic acids.

$$\underset{\text{Trimethyl-carbinol.}}{2(C^4H^{10}O)} + \underset{\text{Oxygen.}}{4O^2} = \underset{\text{Formic acid.}}{2(CH^2O^2)} + \underset{\text{Propionic acid.}}{2(C^3H^6O^2)} + \underset{\text{Water.}}{2(H^2O)}$$

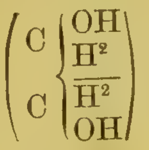
## BIATOMIC ALCOHOLS OR GLYCOLS.

The glycols or biatomic alcohols are derived from hydrocarbides by the substitution of two atoms of hydroxyl for two atoms of hydrogen:



$$\left(\begin{matrix}C\\C\end{matrix}\begin{cases}H^3\\\overline{H^3}\end{cases}\right)$$

Hydride of ethyl.



$$\left(\begin{matrix}C\\ \\C\end{matrix}\begin{cases}OH\\H^2\\\overline{H^2}\\OH\end{cases}\right)$$

Ethyl-glycol.

Preparation.—The glycols may be obtained by four processes:

*First Process.*—Bromine is made to act on a non-oxygenated organic radicle which is capable of furnishing a bibromide: this bibromide is then treated by acetate of potassium in alcoholic solution, or by acetate of silver, when a metallic bromide is formed, and each atom of bromine is replaced by the residue ($C^2H^3O^2$) of the acetate. The body thus formed is a compound ether which, when saponified by a base, furnishes a glycol:

1st. $$\underset{\text{Ethylene.}}{\left(C^2H^{4\prime\prime}\right)} + \underset{\text{Bromine.}}{\left.\begin{matrix}Br\\Br\end{matrix}\right\}} = \underset{\text{Bromide of ethylene.}}{\left(C^2H^4Br^2\right)}$$

2nd. $$\underset{\text{Bromide of ethylene.}}{\left(C^2H^4Br^2\right)} + 2\underset{\text{Acetate of silver.}}{\left(\left.\begin{matrix}C^2H^3O\\Ag\end{matrix}\right\}O\right)} = 2\underset{\text{Bromide of silver.}}{\left(\left.\begin{matrix}Ag\\Br\end{matrix}\right\}\right)} + \underset{\text{Diacetic glycol.}}{\left(C^2H^{4\prime\prime}\left\{\begin{matrix}OC^2H^3O\\OC^2H^3O\end{matrix}\right.\right)}$$

3rd. $$\underset{\text{Diacetic glycol.}}{\left(C^2H^{4\prime\prime}\left\{\begin{matrix}OC^2H^3O\\OC^2H^3O\end{matrix}\right.\right)} + 2\underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = 2\underset{\text{Acetate of potassium.}}{\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right)}$$

$$+ \underset{\text{Glycol.}}{\left(C^2H^{4\prime\prime}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)}$$

Although the bromides used in the preparation of the glycols which are obtained by direct synthesis, are isomeric, and not identical with the bibrominated products of substitution furnished by the saturated hydrocarbides, it is possible, in certain particular cases, to substitute these bromides for one another. M. Caventou has obtained ordinary glycol by employing brominated bromide of ethyl (bibrominated hydride of ethyl) instead of the bromide of ethylene.

*Second Process.*—Hydrogen is substituted for chlorine in the monochlorhydrins of triatomic alcohols. This substitution takes place by the action of nascent hydrogen :

$$\underset{\text{Monochlorhydrin of glycerine.}}{\left(C^3H^{5\prime\prime\prime}\left\{\begin{matrix}Cl\\OH\\OH\end{matrix}\right.\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}} = \underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Propyl-glycol.}}{\left(C^3H^{6\prime\prime}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)}$$

*Third Process.*—A biatomic hydrocarbon radicle is heated with hypochlorous acid. Direct combination takes place, and a monochlorhydric ether is obtained, which when submitted to the action of acetate of silver, furnishes a monacetic ether. This latter, saponified by potash, gives a glycol :

1st. $$\underset{\text{Ethylene.}}{\left(C^2H^{4\prime\prime}\right)} + \underset{\text{Hypochlorous acid.}}{\left(\left.\begin{matrix}Cl\\H\end{matrix}\right\}O\right)} = \underset{\text{Monochlorhydrin of glycol.}}{\left(C^2H^{4\prime\prime}\left\{\begin{matrix}OH\\Cl\end{matrix}\right.\right)}$$

2nd. $$\underset{\text{Monochlorhydrin of glycol.}}{\left(C^2H^{4\prime\prime}\left\{\begin{matrix}OH\\Cl\end{matrix}\right.\right)} + \underset{\text{Acetate of silver.}}{\left(\left.\begin{matrix}C^2H^3O\\Ag\end{matrix}\right\}O\right)} = \underset{\text{Chloride of silver.}}{\left(\left.\begin{matrix}Ag\\Cl\end{matrix}\right\}\right)} + \underset{\text{Monacetic glycol.}}{\left(C^2H^{4\prime\prime}\left\{\begin{matrix}OH\\OC^2H^3O\end{matrix}\right.\right)}$$

3rd. $$\underset{\text{Monacetic glycol.}}{\left(C^2H^{4\prime\prime}\left\{\begin{matrix}OH\\OC^2H^3O\end{matrix}\right.\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Acetate of potassium.}}{\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right)} + \underset{\text{Glycol.}}{\left(C^2H^{4\prime\prime}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)}$$

PROPERTIES.—Glycols agree in most of their properties with monatomic alcohols, but they can undergo those substitutions twice which monatomic alcohols can only undergo once.

1st. *Action of Oxidizing Agents.*—The glycols may lose two or four atoms of hydrogen and thereby give rise to two different aldehyds. They can also exchange two or four atoms of hydrogen for one or two atoms of oxygen and produce two acids:

$$\underset{\text{Glycol.}}{2(C^2H^6O^2)} + \underset{\text{Oxygen.}}{O^2} = \underset{\text{Water.}}{2(H^2O)} + \underset{\substack{\text{Aldehyd of the}\\ \text{first degree.}}}{2(C^2H^4O^2)}$$

$$\underset{\text{Glycol.}}{(C^2H^6O^2)} + \underset{\text{Oxygen.}}{O^2} = \underset{\text{Water.}}{2(H^2O)} + \underset{\substack{\text{Aldehyd of the}\\ \text{second degree.}}}{(C^2H^2O^2)}$$

$$\underset{\text{Glycol.}}{(C^2H^6O^2)} + \underset{\text{Oxygen.}}{O^2} = \underset{\text{Water.}}{(H^2O)} + \underset{\substack{\text{Acid of the}\\ \text{first degree.}}}{(C^2H^4O^3)}$$

$$\underset{\text{Glycol.}}{(C^2H^6O^2)} + \underset{\text{Oxygen.}}{O^4} = \underset{\text{Water.}}{2(H^2O)} + \underset{\substack{\text{Acid of the}\\ \text{second degree.}}}{(C^2H^2O^4)}$$

Very few aldehyds derived from the glycols are as yet known, but it is probable they will soon be obtained.

2nd. *Action of Dehydrating Agents.*—Dehydrants do not reduce the glycols to hydrocarbides, they only subtract a molecule of water from them. The product of this dehydration, instead of being the true anhydride of glycol, is only an isomer.

3rd. *Action of Alkaline Metals.*—Alkaline metals act on glycols in the same manner as on monatomic alcohols, that is to say, they displace the typical hydrogen of these bodies and are themselves substituted in its place. Two products of substitution may be obtained; one containing one atom of the alkaline metal, and another which contains two. On treating these metallic derivatives with the hydriodic ether of a monatomic alcohol, the alcoholic ethers of the glycols are obtained:

$$\underset{\text{Bipotassic glycol.}}{\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\ K^2\end{matrix}\right\}O^2\right)} + 2\underset{\text{Iodide of ethyl.}}{\left(\left.\begin{matrix}C^2H^5\\ I\end{matrix}\right\}\right)} = 2\underset{\substack{\text{Iodide of}\\ \text{potassium.}}}{\left(\left.\begin{matrix}K\\ I\end{matrix}\right\}\right)} + \underset{\substack{\text{Diethylene of}\\ \text{glycol.}}}{\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\ (C^2H^5)^2\end{matrix}\right\}O^2\right)}$$

4th. *Boiling point of the Glycols.*—The glycols present this singular characteristic, that their boiling point becomes lower as their molecular complication augments. This anomaly ends with amyl-glycol. In the glycols above it, the boiling point rises as usual with the complication of the molecule.

5th. *Action of Acids.*—Oxyacids when heated in closed vessels with the glycols give rise to a double decomposition which is exactly like that which takes place with monatomic alcohols. But here, according to the quantity of acid employed, either a single acid radicle may be substituted for a single atom of hydrogen, when a monacid ether is obtained; or two acid radicles may be substituted for two atoms of hydrogen, and then a biacid or neutral ether is the result. In a biacid ether, the two radicles substituted for the hydrogen may belong to a single acid or to two different acids :

$$\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\H^2\end{matrix}\right\}O^2\right) + \left(\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}C^2H^{4\prime\prime}\\C^2H^3O\\H\end{matrix}\right\}O^2\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

Glycol. Acetic acid. Monacetine of glycol. Water.

$$\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\C^2H^3O\\H\end{matrix}\right\}{}^2\right) + \left(\left.\begin{matrix}C^4H^7O\\H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}C^2H^{4\prime\prime}\\C^2H^3O\\C^4H^7O\end{matrix}\right\}O^2\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

Monacetine of glycol. Butyric acid. Butyro-acetine of glycol. Water.

The hydracids act in the same manner as the oxyacids, that is to say, they combine with the glycols, eliminating water, so that a group (HO) in the glycol is replaced by the radicle of the hydracid. Their action, however, does not go beyond this. The ether of the first substitution once obtained, it is not possible, however we may prolong the operation, to give rise to the formation of a biacid ether :

$$\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\H^2\end{matrix}\right\}O^2\right) + \left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right) = \left(C^2H^{4\prime\prime}\left\{\begin{matrix}Cl\\OH\end{matrix}\right.\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

Glycol. Hydrochloric acid. Chlorhydrin. Water.

The biacid ether which would result from the substitution of an atom of a halogen metalloid for the residue (HO) which the monacid ether still contains may, however, be obtained. It is prepared by treating glycol or its simple monacid ethers by the chlorides, bromides, or iodides of phosphorus :

$$\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\H^2\end{matrix}\right\}O^2\right) + 2(PCl^5) = 2(PCl^3O) + 2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right) + \left(\left.\begin{matrix}C^2H^{4\prime\prime}\\Cl^2\end{matrix}\right\}\right)$$

Glycol. Perchloride of phosphorus. Oxychloride of phosphorus. Hydrochloric acid. Dichlorhydrin.

The ethers thus obtained are identical with the chlorides, bromides, or iodides prepared directly by means of a biatomic radicle and chlorine, bromine, or iodine.

6th. *Action of Bases on Ethers and Glycols.*—The compound ethers of the glycols, whether monacid or biacid, are saponified by bases in the same manner as the ethers of monatomic alcohols. This is not the case with simple ethers, which, when submitted to the action of powerful bases, lose an atom of hydrochloric acid. If the monacid ether be used, the anhydride of glycol is produced :

$$\left(C^2H^{4\prime\prime}\left\{\begin{matrix}Cl\\OH\end{matrix}\right.\right) + \left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + \left(C^2H^{4\prime\prime}O\right)$$

Monochlorhydrin. Potash. Chloride of potassium. Water. Oxide of ethylene.

7th. *Properties of the Anhydrides.*—The anhydrides which are formed in the preceding reaction possess remarkable properties.

α. They can unite with water and reconstitute the glycol:

$$\underset{\text{Oxide of ethylene}}{\left(C^2H^4O\right)} + \underset{\text{Water.}}{\left(H^2O\right)} = \underset{\text{Glycol.}}{\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\ H^2\end{matrix}\right\}O^2\right)}$$

β. They can combine directly with ammonia, forming products which will be presently studied in detail. (*See* Ammoniacal Compounds derived from Biatomic Alcohols).

γ. They can enter into double decomposition with metallic salts dissolved in water, in the same way as powerful bases, liberating a hydrate of the metal and giving an ether of the glycol:

$$2\underset{\substack{\text{Oxide of}\\ \text{ethylene.}}}{\left(C^2H^4O\right)} + \underset{\substack{\text{Chloride}\\ \text{of magnesium.}}}{\left(\left.\begin{matrix}Mg^{\prime\prime}\\ Cl^2\end{matrix}\right\}\right)} + 2\underset{\text{Water.}}{\left(H^2O\right)} = \underset{\substack{\text{Hydrate of}\\ \text{magnesium.}}}{\left(\left.\begin{matrix}Mg\\ H^2\end{matrix}\right\}O^2\right)} + 2\underset{\text{Monochlorhydrin.}}{\left(\begin{matrix}\left.\begin{matrix}C^2H^{4\prime\prime}\\ H\end{matrix}\right\}O\\ Cl\end{matrix}\right)}$$

δ. They combine with acids, both hydrated and anhydrous. In the first case a monacid ether, and in the second a biacid ether is produced:

$$\underset{\substack{\text{Oxide of}\\ \text{ethylene.}}}{\left(C^2H^4O\right)} + \underset{\text{Acetic acid.}}{\left(\left.\begin{matrix}C^2H^3O\\ H\end{matrix}\right\}O\right)} = \underset{\text{Monacetic glycol.}}{\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\ C^2H^3O\\ H\end{matrix}\right\}O^2\right)}$$

$$\underset{\substack{\text{Oxide of}\\ \text{ethylene.}}}{\left(C^2H^4O\right)} + \underset{\text{Acetic anhydride.}}{\left(\left.\begin{matrix}C^2H^3O\\ C^2H^3O\end{matrix}\right\}O\right)} = \underset{\text{Diacetic glycol.}}{\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\ (C^2H^3O)^2\end{matrix}\right\}O^2\right)}$$

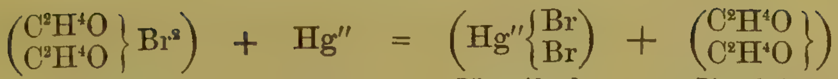
ε. They can also combine with nascent hydrogen, and give the monatomic alcohol of the same series:

$$\underset{\substack{\text{Oxide of}\\ \text{ethylene.}}}{(C^2H^4O)} + \underset{\text{Hydrogen.}}{H^2} = \underset{\text{Alcohol.}}{(C^2H^6O)}$$

The transformation of glycol into the alcohol of the same series may also be made by means of chlorhydrin. This compound exchanges its chlorine directly for hydrogen, and furnishes alcohol. (*See* Preparation of Alcohols).

ζ. Finally, the anhydrides of glycols unite directly with two atoms of bromine, doubling their molecule. The product formed is crystallized. When agitated with mercury, it gives up its bromine, and there remains the original anhydride doubled:

$$2\underset{\substack{\text{Oxide of}\\ \text{ethylene.}}}{\left(C^2H^4O\right)} + \underset{\text{Bromine.}}{\left.\begin{matrix}Br\\ Br\end{matrix}\right\}} = \underset{\substack{\text{Bromide of oxide}\\ \text{of ethlyene.}}}{\left(\left.\begin{matrix}C^2H^4O\\ C^2H^4O\end{matrix}\right\}Br^2\right)}$$



$$\left(\left.\begin{matrix}C^2H^4O\\C^2H^4O\end{matrix}\right\}Br^2\right) + Hg'' = \left(Hg''\left\{\begin{matrix}Br\\Br\end{matrix}\right.\right) + \left(\left.\begin{matrix}C^2H^4O\\C^2H^4O\end{matrix}\right\}\right)$$

Bromide of oxide of ethylene. Mercury. Bibromide of mercury. Dioxethylene.

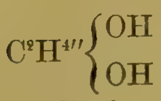
These different properties have only been observed in the anhydride of ordinary glycol. The anhydrides of the other glycols are known, but have not been studied. It appears that they enter into combination less readily in proportion as their molecule becomes complicated. Thus, according to M. Baüer, the oxide of amylene will not unite with water to reconstitute amyl-glycol.

**Condensed Glycols.**—We have seen in mineral chemistry that oxygenized compounds containing several atoms of typical hydrogen can unite with one another, eliminating ($H^2O$) at each addition of a molecule of the polyatomic body.

This fact, examples of which have been given when speaking of phosphoric and sulphuric acids, was first discovered in the glycols, where it is presented with great clearness. The condensed glycols represent simple glycols to which molecules of anhydrides of glycols have been added.

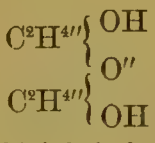
In order to understand their formation, it must be admitted that two molecules of a biatomic alcohol lose, the one H, and the other OH to form water; two monatomic residues are the result, and these unite to form a condensed glycol. The oxygen of the residue of the water which has lost its hydrogen serves to unite the two hydrocarbon molecules. As each condensation is accompanied by the elimination of ($H^2O$), the condensed glycols all contain two hydroxyls like the simple glycols.

At present, five products of condensation derived from ordinary glycol are known, the rational formulæ of which are as follows:



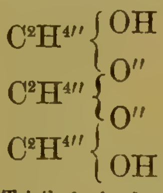
$$C^2H^{4''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.$$

Glycol.



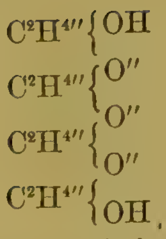
$$\begin{array}{ll} C^2H^{4''} & \{\,OH \\ & \;\;O'' \\ C^2H^{4''} & \{\,OH \end{array}$$

Diethylenic glycol.



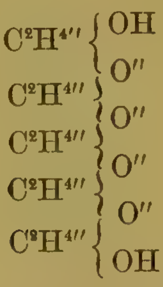
$$\begin{array}{ll} C^2H^{4''} & \{\,OH \\ & \;\;O'' \\ C^2H^{4''} & \{ \\ & \;\;O'' \\ C^2H^{4''} & \{\,OH \end{array}$$

Triethylenic glycol.



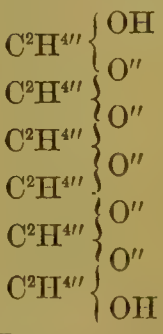
$$\begin{array}{ll} C^2H^{4''} & \{\,OH \\ & \;\;O'' \\ C^2H^{4''} & \{ \\ & \;\;O'' \\ C^2H^{4''} & \{ \\ & \;\;O'' \\ C^2H^{4''} & \{\,OH \end{array}$$

Tetrethylenic glycol.



$$\begin{array}{ll} C^2H^{4''} & \{\,OH \\ & \;\;O'' \\ C^2H^{4''} & \{ \\ & \;\;O'' \\ C^2H^{4''} & \{ \\ & \;\;O'' \\ C^2H^{4''} & \{ \\ & \;\;O'' \\ C^2H^{4''} & \{\,OH \end{array}$$

Pentethylenic glycol.

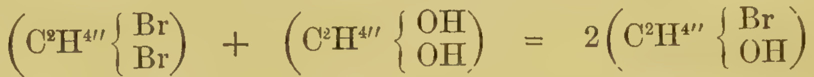


$$\begin{array}{ll} C^2H^{4''} & \{\,OH \\ & \;\;O'' \\ C^2H^{4''} & \{ \\ & \;\;O'' \\ C^2H^{4''} & \{ \\ & \;\;O'' \\ C^2H^{4''} & \{ \\ & \;\;O'' \\ C^2H^{4''} & \{ \\ & \;\;O'' \\ C^2H^{4''} & \{\,OH \end{array}$$

Hexethylenic glycol.

Preparation of the Condensed Glycols.—Three processes have been used to obtain these compounds.

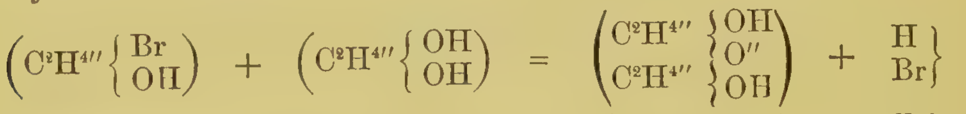
*First.*—A simple ether of a glycol is heated in a hermetically-sealed tube with the glycol itself. If the ether employed be biacid, it will first be transformed into monacid ether on contact with the glycol:



$$\left(C^2H^{4''}\left\{\begin{matrix}Br\\Br\end{matrix}\right.\right) + \left(C^2H^{4''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right) = 2\left(C^2H^{4''}\left\{\begin{matrix}Br\\OH\end{matrix}\right.\right)$$

Bromide of ethylene. Glycol. Monobromhydrin.

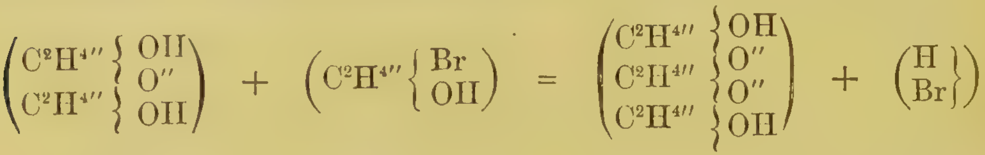
The monacid ether formed then enters into double decomposition with the remaining glycol; a condensed alcohol is produced as well as hydrobromic acid:



$$\left(C^2H^{4''}\left\{\begin{matrix}Br\\OH\end{matrix}\right.\right) + \left(C^2H^{4''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right) = \left(\begin{matrix}C^2H^{4''}\\ \\ C^2H^{4''}\end{matrix}\begin{matrix}\}OH\\ \}O''\\ \}OH\end{matrix}\right) + \left.\begin{matrix}H\\Br\end{matrix}\right\}$$

Monobromhydrin. Glycol. Diethylenic glycol. Hydrobromic acid.

The hydrobromic acid reacts on another portion of the glycol, and reconstitutes bromhydrin, which, on contact with the condensed alcohol already formed, produces an alcohol of greater condensation:

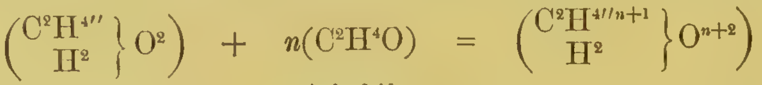


$$\left(\begin{matrix}C^2H^{4''}\\ \\ C^2H^{4''}\end{matrix}\begin{matrix}\}OH\\ \}O''\\ \}OH\end{matrix}\right) + \left(C^2H^{4''}\left\{\begin{matrix}Br\\OH\end{matrix}\right.\right) = \left(\begin{matrix}C^2H^{4''}\\ \\ C^2H^{4''}\\ \\ C^2H^{4''}\end{matrix}\begin{matrix}\}OH\\ \}O''\\ \\ \}O''\\ \}OH\end{matrix}\right) + \left(\left.\begin{matrix}H\\Br\end{matrix}\right\}\right)$$

Diethylenic glycol. Monobromhydrin. Triethylenic glycol. Hydrobromic acid.

And the reaction is thus continued without our being able to assign any limit to the condensation.

*Second Process.*—A glycol is heated with its anhydride for a fortnight. The products of condensation then form by direct synthesis:

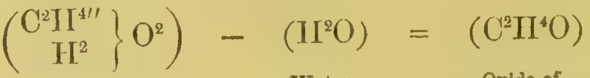


$$\left(\left.\begin{matrix}C^2H^{4''}\\H^2\end{matrix}\right\}O^2\right) + n(C^2H^4O) = \left(\left.\begin{matrix}C^2H^{4''n+1}\\H^2\end{matrix}\right\}O^{n+2}\right)$$

Glycol. Anhydride of glycol.

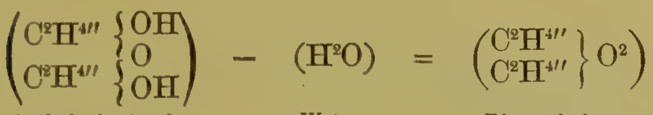
*Third Process.*—The oxide of ethylene is heated with an acid; a compound ether of the simple glycol is first formed, which afterwards combines successively with one, two, three, four . . . *n* molecules of the anhydride remaining, and produces compound ethers of the different condensed glycols. These ethers, when saponified by a base, give the condensed glycols of which they contain the elements.

Properties.—1st. All condensed glycols possess the same number of atoms of typical hydrogen as the simple alcohol from which they are derived, that is to say, two. They act as biatomic alcohols, and give an anhydride and two series of ethers. The dioxyethylene may be regarded as the anhydride of the diethylenic glycol:



$$\left(\left.\begin{matrix}C^2H^{4''}\\H^2\end{matrix}\right\}O^2\right) - (H^2O) = (C^2H^4O)$$

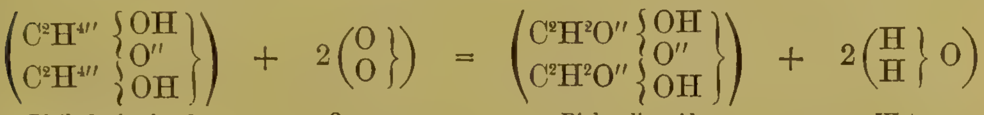
Glycol. Water. Oxide of ethylene.



$$\left(\begin{matrix}C^2H^{4\prime\prime}\\C^2H^{4\prime\prime}\end{matrix}\left\{\begin{matrix}OH\\O\\OH\end{matrix}\right.\right) - (H^2O) = \left(\left.\begin{matrix}C^2H^{4\prime\prime}\\C^2H^{4\prime\prime}\end{matrix}\right\}O^2\right)$$

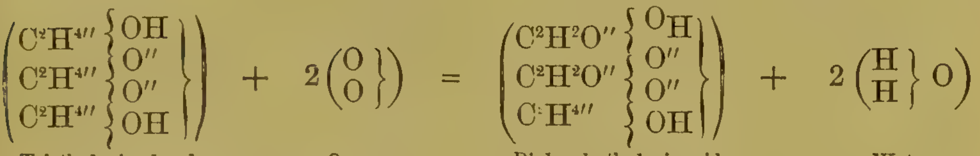
Diethylenic glycol. Water. Dioxyethylene.

2nd. Like simple glycols, the condensed glycols can exchange hydrogen for oxygen, and give rise to acids. Up to the present time this property has only been observed in the diethylenic and triethylenic glycols. In these two cases, four atoms of hydrogen have been replaced by two of oxygen :



$$\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\C^2H^{4\prime\prime}\end{matrix}\left\{\begin{matrix}OH\\O^{\prime\prime}\\OH\end{matrix}\right.\right\}\right) + 2\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\right) = \left(\left.\begin{matrix}C^2H^2O^{\prime\prime}\\C^2H^2O^{\prime\prime}\end{matrix}\left\{\begin{matrix}OH\\O^{\prime\prime}\\OH\end{matrix}\right.\right\}\right) + 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

Diethylenic glycol. Oxygen. Diglycolic acid. Water.



$$\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\C^2H^{4\prime\prime}\\C^2H^{4\prime\prime}\end{matrix}\left\{\begin{matrix}OH\\O^{\prime\prime}\\O^{\prime\prime}\\OH\end{matrix}\right.\right\}\right) + 2\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\right) = \left(\left.\begin{matrix}C^2H^2O^{\prime\prime}\\C^2H^2O^{\prime\prime}\\C^2H^{4\prime\prime}\end{matrix}\left\{\begin{matrix}OH\\O^{\prime\prime}\\O^{\prime\prime}\\OH\end{matrix}\right.\right\}\right) + 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

Triethylenic glycol. Oxygen. Diglycol-ethylenic acid. Water.

These facts appear to demonstrate that, in condensed as in simple glycols, the maximum quantity of oxygen which can be substituted for hydrogen is two atoms.

**Enumeration of the known Glycols.**—Up to the present time six glycols are know with certainty. These are :

| | |
|---|---|
| Ordinary, or ethylglycol . . . . . . | $\left.\begin{matrix}C^2H^{4\prime\prime}\\H^2\end{matrix}\right\}O^2$ |
| Propylglycol . . . . . . . . . | $\left.\begin{matrix}C^3H^{6\prime\prime}\\H^2\end{matrix}\right\}O^2$ |
| Butylglycol . . . . . . . . . | $\left.\begin{matrix}C^4H^{8\prime\prime}\\H^2\end{matrix}\right\}O^2$ |
| Amylglycol . . . . . . . . . | $\left.\begin{matrix}C^5H^{10\prime\prime}\\H^2\end{matrix}\right\}O^2$ |
| Hexylglycol . . . . . . . . . | $\left.\begin{matrix}C^6H^{12\prime\prime}\\H^2\end{matrix}\right\}O^2$ |
| Octylglycol . . . . . . . . . | $\left.\begin{matrix}C^8H^{16\prime\prime}\\H^2\end{matrix}\right\}O^2$ |

Besides these, two bodies are known which have the composition of hexylglycol $\left(\left.\begin{matrix}C^6H^{12\prime\prime}\\H^2\end{matrix}\right\}O^2\right)$. These are, a product derived from allyl, and one derived from acetone which is called pinakone; the first of these bodies is a simple isomer of the true hexylglycol; pinakone has been too little studied for its composition to be determined with certainty.

There also exists a body which corresponds to the formula $(C^{10}H^{20}O)$.

This body has been prepared by means of decylene ($C^{10}H^{20}$) by a process identical with that which furnishes the lower glycols of the series. There is, therefore, reason to believe that, when the molecule is sufficiently complicated, the glycols cease to be stable, and therefore that only their anhydrides can be obtained. The body ($C^{10}H^{20}O$) may be considered as the anhydride of decylglycol:

$$\left(\left.\begin{matrix}C^{10}H^{20\prime\prime}\\H^2\end{matrix}\right\}O^2\right) - (H^2O) = (C^{10}H^{20}O)$$

Decylglycol (unknown). Water. Oxide of decylene.

Methylenic glycol $\left(\left.\begin{matrix}CH^{2\prime\prime}\\H^2\end{matrix}\right\}O^2\right)$ cannot exist in a free state, owing to the slight stability of its molecule. When iodide of methylene ($CH^2I^2$) is treated with acetate of silver, a diacetic ether of this body is produced. But this does not give methylglycol by saponification.

On causing the oxalate instead of the acetate of silver to act on iodide of methylene, a compound is obtained which appears to be to the unknown oxide of methylene what dioxyethylene is to the oxide of ethylene. This compound has received the name of dioxymethylene, and has for formula $\left(\left.\begin{matrix}CH^{2\prime\prime}\\CH^{2\prime\prime}\end{matrix}\right\}O^2\right)$.

The iodide of methylene used for these experiments cannot be obtained by the action of iodine on methylene, which does not exist; it is produced in a complex reaction, when ethylate of sodium is treated by iodine.

**Action of the Polyatomic Acids on the Glycols.** When polyatomic acids are made to act on glycols, these bodies unite, eliminating water, and acid compounds are produced, which represent condensed glycols, one or more hydrocarbon radicles of which have given place to one or more acid radicles. At a higher temperature these products can still lose water and form anhydrides which, in certain cases, are neutral ethers of the glycols:

$$\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\H^2\end{matrix}\right\}O^2\right) + \left(\left.\begin{matrix}C^4H^4O^{2\prime\prime}\\H^2\end{matrix}\right\}O^2\right) = \left(\begin{matrix}C^2H^{4\prime\prime}\\C^4H^4O^{2\prime\prime}\end{matrix}\left\{\begin{matrix}OH\\O^{\prime\prime}\\OH\end{matrix}\right.\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

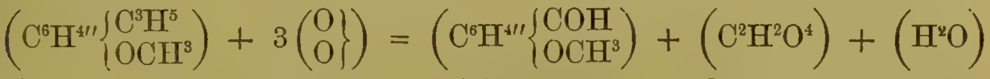
Glycol. Succinic acid. Succino-ethylenic acid. Water.

$$\left(\begin{matrix}C^2H^{4\prime\prime}\\C^4H^4O^{2\prime\prime}\end{matrix}\left\{\begin{matrix}OH\\O^{\prime\prime}\\OH\end{matrix}\right.\right) = \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}C^2H^{4\prime\prime}\\C^4H^4O^2\end{matrix}\right\}O^2\right)$$

Succino-ethylenic acid. Water. Succinic glycol.

## APPENDIX TO THE BIATOMIC ALCOHOLS.

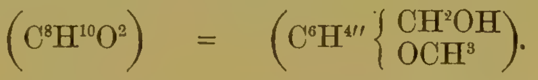
**Anisic Alcohol.**—There exists in aniseed an essence which corresponds to the formula $(C^{10}H^{12}O)$. This essence appears to have a constitution represented by the formula $\left(C^6H^{4'''}\left\{\begin{matrix}C^3H^5\\ OCH^3\end{matrix}\right.\right)$. By oxidation it furnishes a compound the formula of which is $(C^8H^8O^2)$, according to the equation:



$$\underset{\text{Essence of aniseed.}}{\left(C^6H^{4'''}\left\{\begin{matrix}C^3H^5\\ OCH^3\end{matrix}\right.\right)} + \underset{\text{Oxygen.}}{3\left(\left.\begin{matrix}O\\ O\end{matrix}\right\}\right)} = \underset{\text{Anisic aldehyd.}}{\left(C^6H^{4'''}\left\{\begin{matrix}COH\\ OCH^3\end{matrix}\right.\right)} + \underset{\text{Oxalic acid.}}{\left(C^2H^2O^4\right)} + \underset{\text{Water.}}{\left(H^2O\right)}$$

M. Cannizzaro, by submitting this product, which is a true aldehyd, to the action of alcoholic solution of potash, has transformed it into an alcohol which he named anisic alcohol, and which answers to the formula $(C^8H^{10}O^2)$.

This alcohol, though containing two atoms of oxygen like the glycols, acts as a monatomic alcohol. But in reality this compound is none other than monomethylic ether of the unknown benzylglycol:



$$\underset{\text{Anisic alcohol.}}{\left(C^8H^{10}O^2\right)} = \underset{\text{Monomethylic benzylglycol.}}{\left(C^6H^{4'''}\left\{\begin{matrix}CH^2OH\\ OCH^3\end{matrix}\right.\right)}.$$

It is thus easily explained why this body can only furnish a single series of ethers, as it only contains a single atom of typical hydrogen.

## TRIATOMIC ALCOHOLS OR GLYCERINES.

Though, in all probability, there corresponds to each monatomic alcohol a glycol and a glycerine, only two glycerines are as yet known. One is propylglycerine $\left(\left.\begin{matrix}C^3H^{5'''}\\ H^3\end{matrix}\right\}O^3\right)$ and the other amylglycerine $\left(\left.\begin{matrix}C^5H^{9'''}\\ H^3\end{matrix}\right\}O^3\right)$. Besides these, M. Wurtz appears to have recently obtained an acetate $\left(\left.\begin{matrix}C^6H^{11'''}\\ (C^2H^3O)^3\end{matrix}\right\}O^3\right)$, which would, perhaps, furnish hexylglycerine $\left(\left.\begin{matrix}C^6H^{11'''}\\ H^3\end{matrix}\right\}O^3\right)$ by saponification.

Amylic glycerine having been very little studied, all we shall say will relate solely to propylglycerine or ordinary glycerine, unless we specially indicate the contrary.

Triatomic alcohols are derived from a fundamental hydrocarbide by the substitution of three atoms of hydroxyl for three atoms of hydrogen.

Preparation.—Ordinary glycerine is produced during the saponification of natural fatty bodies, which are ethers; in order to obtain it pure, this saponification is made by means of oxide of lead and water. An insoluble salt of lead is formed, and the liberated glycerine is dissolved. A current of sulphuretted hydrogen is transmitted into the solution to precipitate the traces of lead the liquid contains, and it is then filtered and evaporated. The glycerine remains, in the form of a syrupy liquid. Very pure glycerine is obtained on a large scale by saponifying fatty bodies by superheated steam. Glycerine and fatty acids distil. On cooling, the fatty acid, which forms a solid layer on the surface of the distilled liquid, is removed, the liquid is evaporated, and the glycerine remains.

As yet, glycerine has not been prepared synthetically. It is true that M. Wurtz has been able to reconstitute it by submitting the tribromide of allyl ($C^3H^5Br^3$) to a treatment identical with that which furnishes glycol by means of the bromide of ethylene; but, unfortunately, the tribromide of allyl is derived from glycerine itself, and has not been otherwise prepared.

Amylic glycerine is obtained synthetically. The bromide of brominated amylene, when submitted to the action of acetate of silver, gives rise to the diacetic ether of monobrominated amylglycol; this ether, saponified by potash, furnishes monobrominated amylglycol. Finally, the monobrominated amylglycol, heated with potash, is transformed into amylglycerine, and bromide of potassium and water are formed:

1st.

$$\left(\left.\begin{matrix}C^5H^9Br''\\ Br^2\end{matrix}\right\}\right) + 2\left(\left.\begin{matrix}C^2H^3O\\ Ag\end{matrix}\right\}O\right) = 2\left(\left.\begin{matrix}Ag\\ Br\end{matrix}\right\}\right) + \left(\left.\begin{matrix}C^5H^9Br''\\ (C^2H^3O)^2\end{matrix}\right\}O^2\right)$$

Bromide of brominated amylene. — Acetate of silver. — Bromide of silver. — Brominated diacetic amylglycol.

2nd.

$$\left(\left.\begin{matrix}C^5H^9Br''\\ (C^2H^3O)^2\end{matrix}\right\}O^2\right) + 2\left(\left.\begin{matrix}K\\ H\end{matrix}\right\}O\right) = 2\left(\left.\begin{matrix}C^2H^3O\\ K\end{matrix}\right\}O\right)$$

Brominated diacetic amylglycol. — Potash. — Acetate of potassium.

$$+ \left(\left.\begin{matrix}C^5H^9Br''\\ H^2\end{matrix}\right\}O^2\right)$$

Monobrominated amylglycol.

3rd.

$$\left(\left.\begin{matrix}C^5H^9Br''\\ H^2\end{matrix}\right\}O^2\right) + \left(\left.\begin{matrix}K\\ H\end{matrix}\right\}O\right) = \left.\begin{matrix}K\\ Br\end{matrix}\right\} + \left(\left.\begin{matrix}C^5H^{9'''}\\ H^3\end{matrix}\right\}O^3\right)$$

Monobrominated amylglycol. — Hydrate of potassium. — Bromide of potassium. — Amylglycerine.

PROPERTIES.—Triatomic alcohols are very similar in their properties to biatomic alcohols. The chief difference between them is, that where the glycols give two derivatives these give three.

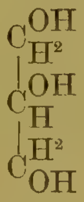
1st. *Oxidizing Agents.*—Oxidants, on reacting on glycerine, produce several acids. One of them has been studied, and results from the substitution of O for $H^2$ in the radicle; it is glyceric acid:

$$\left(\left.\begin{matrix}C^3H^{5'''}\\ H^3\end{matrix}\right\}O^3\right) + \left.\begin{matrix}O\\ O\end{matrix}\right\} = \left(\left.\begin{matrix}C^3H^3O'''\\ H^3\end{matrix}\right\}O^3\right) + \left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)$$

Glycerine. — Oxygen. — Glyceric acid. — Water.

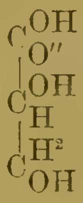
It is probable that an acid resulting from the substitution of $O^2$ for $H^4$ might be obtained. Analogy appears to indicate that with glycerines whose radicle contains sufficient hydrogen, such as amylglycerine for instance, three atoms of oxygen ought to be able to be substituted for six atoms of hydrogen.

Such a substitution would only, however, be possible in the secondary and tertiary glycerines; primary glycerines, the only ones known, result from the substitution of 3OH for 3H in a hydrocarbide. Of these three OH, the two at the extremities have two atoms of hydrogen near them, and that in the centre has only one, as the following formula shows:



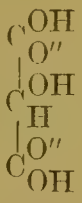
$$\begin{array}{l}\mathrm{C}\begin{array}{l}\mathrm{OH}\\\mathrm{H^2}\end{array}\\ |\\ \mathrm{C}\begin{array}{l}\mathrm{OH}\\\mathrm{H}\end{array}\\ |\\ \mathrm{C}\begin{array}{l}\mathrm{H^2}\\\mathrm{OH}\end{array}\end{array}$$

Thus, as acids result from the substitution of O for $H^2$ near the hydroxyl, this substitution would be possible in the two outer atoms but not in the middle one, and two acids only could be obtained with glycerine:



$$\begin{array}{l}\mathrm{C}\begin{array}{l}\mathrm{OH}\\\mathrm{O''}\end{array}\\ |\\ \mathrm{C}\begin{array}{l}\mathrm{OH}\\\mathrm{H}\end{array}\\ |\\ \mathrm{C}\begin{array}{l}\mathrm{H^2}\\\mathrm{OH}\end{array}\end{array}$$

and



$$\begin{array}{l}\mathrm{C}\begin{array}{l}\mathrm{OH}\\\mathrm{O''}\end{array}\\ |\\ \mathrm{C}\begin{array}{l}\mathrm{OH}\\\mathrm{H}\end{array}\\ |\\ \mathrm{C}\begin{array}{l}\mathrm{O''}\\\mathrm{OH}\end{array}\end{array}$$

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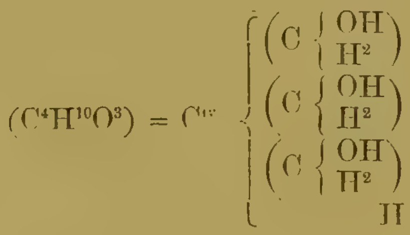
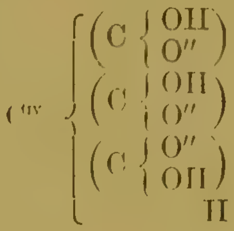
This would no longer be the case with a tertiary glycerine:



$$(\mathrm{C^4H^{10}O^3}) = \mathrm{C^{iv}}\left\{\begin{array}{l}\left(\mathrm{C}\left\{\begin{array}{l}\mathrm{OH}\\\mathrm{H^2}\end{array}\right.\right)\\ \left(\mathrm{C}\left\{\begin{array}{l}\mathrm{OH}\\\mathrm{H^2}\end{array}\right.\right)\\ \left(\mathrm{C}\left\{\begin{array}{l}\mathrm{OH}\\\mathrm{H^2}\end{array}\right.\right)\\ \qquad\quad \mathrm{H}\end{array}\right.$$

Here the three atoms of hydroxyl having $H^2$ near them, the substitution of O for $H^2$ could take place three times, and the triatomic and tribasic acid



$$\mathrm{C^{iv}}\left\{\begin{array}{l}\left(\mathrm{C}\left\{\begin{array}{l}\mathrm{OH}\\\mathrm{O''}\end{array}\right.\right)\\ \left(\mathrm{C}\left\{\begin{array}{l}\mathrm{OH}\\\mathrm{O''}\end{array}\right.\right)\\ \left(\mathrm{C}\left\{\begin{array}{l}\mathrm{O''}\\\mathrm{OH}\end{array}\right.\right)\\ \qquad\quad \mathrm{H}\end{array}\right.$$

would be possible.

No glyceric aldehyd is known as yet.

2nd. *Dehydrating Agents.*—When glycerine is heated with a body having great affinity for water, it loses $2(H^2O)$ and a liquid distils, which is acrolein, and the formula of which is $(C^3H^4O)$. Acrolein ought to be classed with the aldehyds, and not in the glycerine series.

3rd. *Action of Alkaline Metals.*—When a piece of sodium is placed in glycerine, hydrogen is disengaged, but the mass soon becomes pasty, and all reaction is arrested. It is probable that if, by means of a solvent, the mass could be rendered more fluid, it would be possible to substitute one, two, or three atoms of sodium for one, two, or three atoms of hydrogen. In effecting this the solvent ought, of course, to exercise no action on the alkaline metal.

4th. *Action of Bases.*—Bases combine directly with glycerine, but the compounds appear to have more relation to those resulting from the union of the water of crystallization with a salt, than to true atomic combinations.

5th. *Actions of Monatomic Oxyacids.*—When quantities of glycerine and of a monatomic acid, respectively proportional to the molecular weights of these bodies, are heated in a closed vessel, a double decomposition takes place; one atom of hydrogen is replaced by the radicle of the acid used, and a monacid compound ether of glycerine is produced:

$$\underset{\text{Glycerine.}}{\left(\left.\begin{matrix}C^3H^{5'''}\\H^3\end{matrix}\right\}O^3\right)} + \underset{\text{Benzoic acid.}}{\left(\left.\begin{matrix}C^7H^5O\\H\end{matrix}\right\}O\right)} = \underset{\text{Monobenzoate of glycerine.}}{\left(\left.\begin{matrix}C^3H^{5'''}\\C^7H^5O\\H^2\end{matrix}\right\}O^3\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

If the monacid ether be heated with another quantity of the same acid, or with an equivalent quantity of a different acid, a biacid ether is produced by a reaction identical with the preceding:

$$\underset{\text{Monobenzoicin.}}{\left(\left.\begin{matrix}C^3H^{5'''}\\H^2\\C^7H^5O\end{matrix}\right\}O^3\right)} + \underset{\text{Acetic acid.}}{\left(\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O\right)} = \underset{\text{Aceto-benzoicin.}}{\left(\left.\begin{matrix}C^3H^{5'''}\\C^2H^3O\\C^7H^5O\\H\end{matrix}\right\}O^3\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

Finally, these ethers of the second degree, when heated a third time with a fresh proportion of acid, furnish ethers of three acid radicles.

$$\underset{\text{Aceto-benzoicin.}}{\left(\left.\begin{matrix}C^3H^{5'''}\\C^2H^3O\\C^7H^5O\\H\end{matrix}\right\}O^3\right)} + \underset{\text{Butyric acid.}}{\left(\left.\begin{matrix}C^4H^7O\\H\end{matrix}\right\}O\right)} = \underset{\text{Aceto-butyro-benzoicin.}}{\left(\left.\begin{matrix}C^3H^{5'''}\\C^2H^3O\\C^7H^5O\\C^4H^7O\end{matrix}\right\}O^3\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

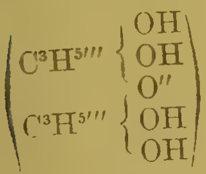
The triacid ethers may be heated indefinitely with new proportions of acid without giving rise to any double decomposition. Glycerine therefore contains only three atoms of typical hydrogen.

n these reactions it is always necessary to recommence the opera-
ı several times. A biacid ether of glycerine could not be prepared
heating directly a molecule of glycerine with two molecules of a
ıatomic acid. In order to succeed, the monacid ether must first be
pared and then treated with a fresh quantity of acid.

ith. *Action of Alcohols.*—Alcohols do not act on glycerine; but if the
drobromic ether of a monatomic alcohol be heated with a glyceric
ution of potash, the replacement of a part of the typical hydrogen
the glycerine by an alcohol radicle takes place: a method will pre-
ıtly be described by which these products may be prepared with
ıch greater certainty.

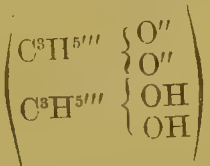
7th. *Action of Hydracids.*—Like oxyacids, the hydracids enter into
ouble decomposition with glycerine; their radicle is substituted for
ıe group HO in this alcohol. As glycerine contains three atoms
hydroxyl, it may be conceived that such a substitution can be pro-
uced three times. Nevertheless, by the action of hydrochloric or
ydrobromic acids on glycerine, it has never been possible to substi-
ıte the chlorine or bromine for the residue (HO) more than twice.

Hydriodic acid, instead of giving a normal ether like its congeners,
ives rise to a product of condensation the formula of which is
$C^6H^{11}O^3$). This product may be considered as the moniodhydrin of
he first anhydride of diglyceric alcohol:



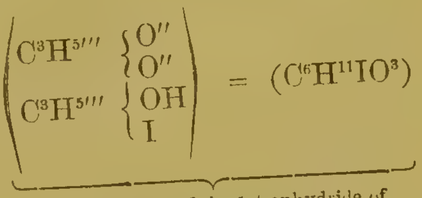
$$\left(\begin{matrix} C^3H^{5'''}\left\{\begin{matrix}OH\\OH\end{matrix}\right. \\ O'' \\ C^3H^{5'''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\end{matrix}\right)$$

Diglyceric alcohol.



$$\left(\begin{matrix} C^3H^{5'''}\left\{\begin{matrix}O''\\O''\end{matrix}\right. \\ C^3H^{5'''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\end{matrix}\right)$$

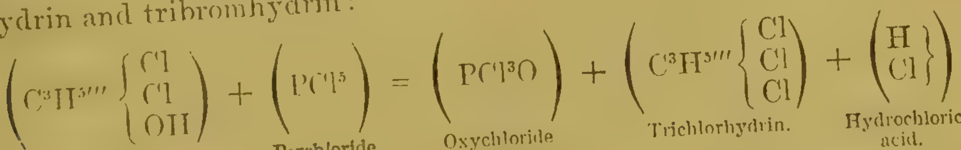
1st anhydride of diglyceric alcohol.



$$\underbrace{\left(\begin{matrix} C^3H^{5'''}\left\{\begin{matrix}O''\\O''\end{matrix}\right. \\ C^3H^{5'''}\left\{\begin{matrix}OH\\I\end{matrix}\right.\end{matrix}\right) = (C^6H^{11}IO^3)}$$

Moniodhydrin of the 1st anhydride of diglyceric alcohol.

8th. *Actions of the Chlorides and Bromides of Phosphorus.*—In acting on glycerine, the perchloride and perbromide of phosphorus produce the same bodies as the corresponding hydracids, but their action extends further. Instead of stopping at the production of dichlorhydrin or dibromhydrin, they transform these latter bodies into trichlorhydrin and tribromhydrin:



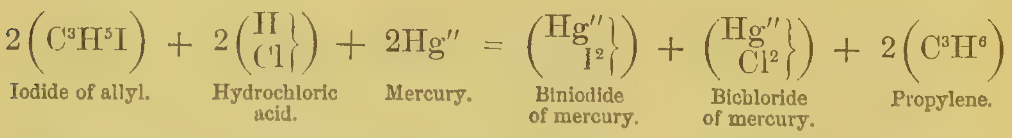
$$\left(C^3H^{5'''}\left\{\begin{matrix}Cl\\Cl\\OH\end{matrix}\right.\right) + \left(PCl^5\right) = \left(PCl^3O\right) + \left(C^3H^{5'''}\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right.\right) + \left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)$$

Dichlorhydrin. Perchloride of phosphorus. Oxychloride of phosphorus. Trichlorhydrin. Hydrochloric acid.

Among the ethers of glycerine just considered, there are some which exist native. These are the ethers with three acid radicles, derived from the oxyacids whose molecules have a certain degree of complication. Such are the ethers of oleic, stearic, margaric, palmitic, and other acids which have received the name of neutral fatty bodies. The natural neutral fats are identical with the artificial ones.

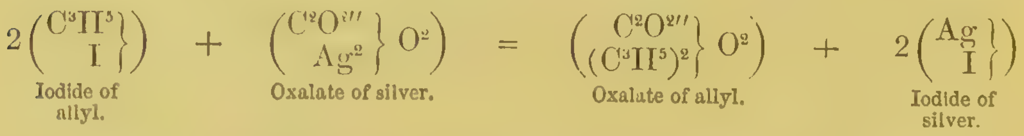
9th. *Action of Iodide of Phosphorus.*—Iodide of phosphorus, acting on glycerine, gives rise to a reaction which is entirely different from that produced by its congeners: iodine is liberated and hydriodic ether of a non-saturated monatomic alcohol is formed, which contains the same radicle ($C^3H^5$) as glycerine. The formula of the iodide thus produced is therefore ($C^3H^5I$); it is called iodide of allyl, and the alcohol to which it corresponds, allylic alcohol.*

When boiled with a mixture of mercury and hydrochloric acid, the iodide of allyl gives propylene, exchanging its atom of iodine for an atom of hydrogen:



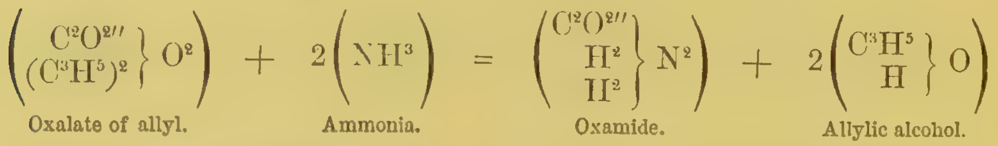
$$2\underset{\text{Iodide of allyl.}}{\left(C^3H^5I\right)} + 2\underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Mercury.}}{2Hg''} = \underset{\text{Biniodide of mercury.}}{\left(\left.\begin{matrix}Hg''\\I^2\end{matrix}\right\}\right)} + \underset{\text{Bichloride of mercury.}}{\left(\left.\begin{matrix}Hg''\\Cl^2\end{matrix}\right\}\right)} + 2\underset{\text{Propylene.}}{\left(C^3H^6\right)}$$

Submitted to the action of oxalate of silver, iodide of allyl gives rise to a double decomposition represented by the following equation:



$$2\underset{\text{Iodide of allyl.}}{\left(\left.\begin{matrix}C^3H^5\\I\end{matrix}\right\}\right)} + \underset{\text{Oxalate of silver.}}{\left(\left.\begin{matrix}C^2O^{2''}\\Ag^2\end{matrix}\right\}O^2\right)} = \underset{\text{Oxalate of allyl.}}{\left(\left.\begin{matrix}C^2O^{2''}\\(C^3H^5)^2\end{matrix}\right\}O^2\right)} + 2\underset{\text{Iodide of silver.}}{\left(\left.\begin{matrix}Ag\\I\end{matrix}\right\}\right)}$$

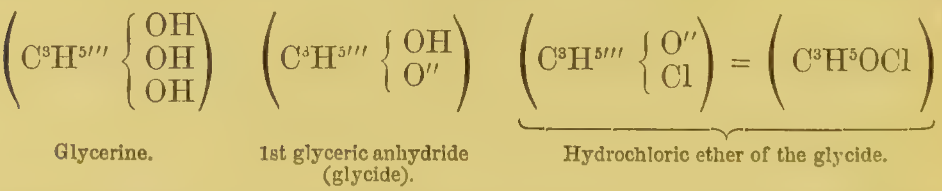
The oxalate of allyl thus produced, decomposes when treated by ammonia, forming oxamide and allylic alcohol:



$$\underset{\text{Oxalate of allyl.}}{\left(\left.\begin{matrix}C^2O^{2''}\\(C^3H^5)^2\end{matrix}\right\}O^2\right)} + 2\underset{\text{Ammonia.}}{\left(NH^3\right)} = \underset{\text{Oxamide.}}{\left(\left.\begin{matrix}C^2O^{2''}\\H^2\\H^2\end{matrix}\right\}N^2\right)} + 2\underset{\text{Allylic alcohol.}}{\left(\left.\begin{matrix}C^3H^5\\H\end{matrix}\right\}O\right)}$$

Finally, bromine displaces the iodine which the iodide of allyl contains and transforms this body into terbromide of allyl ($C^3H^5Br^3$). It is by means of this tribromide of allyl that M. Wurtz has re-formed glycerine.

**Glycide.**—When potash is made to act on glyceric dichlorhydrin, a molecule of hydrochloric acid is eliminated, and a product remains to which M. Berthelot gave the name of epichlorhydrin. M. Reboul has shown that this product ought to be considered as the hydrochloric ether of a first anhydride of glycerine, unknown in the free state and acting as an alcohol. To this unknown anhydride he gave the name of glycide:



$$\underset{\text{Glycerine.}}{\left(C^3H^{5'''}\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.\right)} \quad \underset{\text{1st glyceric anhydride (glycide).}}{\left(C^3H^{5'''}\left\{\begin{matrix}OH\\O''\end{matrix}\right.\right)} \quad \underbrace{\left(C^3H^{5'''}\left\{\begin{matrix}O''\\Cl\end{matrix}\right.\right) = \left(C^3H^5OCl\right)}_{\text{Hydrochloric ether of the glycide.}}$$

The reaction which gives rise to the hydrochloric glycide is represented by the following equation:

---

* Allylic alcohol, because the essence of garlic is the sulphide of allyl.

$$\underset{\text{Dichlorhydrin.}}{\left(C^3H^{5'''}\left\{\begin{matrix}OH\\Cl\\Cl\end{matrix}\right.\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Hydrochloric glycide.}}{\left(C^3H^{5'''}\left\{\begin{matrix}O''\\Cl\end{matrix}\right.\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Chloride of potassium.}}{\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)}$$

On substituting dibromhydrin for dichlorhydrin in the preceding preparation, the hydrobromic glycide ($C^3H^5BrO$) would be obtained. The ethers of glycide have always a tendency to return to the type of the glycerine whence they are derived.

*Action of Hydracids.*—The hydracids combine directly with hydrochloric glycide, forming a simple ether of glycerine having two halogen identical or different radicles:

$$\underset{\text{Hydrochloric glycide.}}{(C^3H^5OCl)} + \underset{\text{Hydrobromic acid.}}{(HBr)} = \underset{\text{Hydrochlorobromhydrin of glycerine.}}{(C^3H^6BrClO)}$$

When heated with dry iodide of potassium, the hydrochloric glycide produces a hydriodic glycide:

$$\underset{\text{Hydrochloric glycide.}}{\left(C^3H^5ClO\right)} + \underset{\text{Iodide of potassium.}}{\left(\left.\begin{matrix}K\\I\end{matrix}\right\}\right)} = \underset{\text{Chloride of potassium.}}{\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)} + \underset{\text{Hydriodic glycide.}}{\left(C^3H^5IO\right)}$$

This latter body, on uniting directly with hydriodic acid, gives rise to glyceric di-iodhydrin, which, as has been already seen, can be obtained by no other process.

The simple ethers of glycerine which are obtained by the action of the hydracids on epichlorhydrin or epibromhydrin re-form these bodies by the action of potash.

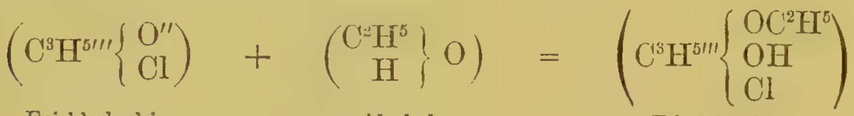
*Action of Oxyacids.*—Oxyacids also unite with epichlorhydrin, but the action requires to be assisted by heat. In this case a mixed ether is formed, as the following equation shows:

$$\underset{\text{Epichlorhydrin.}}{(C^3H^5OCl)} + \underset{\text{Acetic acid.}}{(C^2H^4O^2)} = \underbrace{(C^5H^9ClO^3) = \left(C^3H^{5'''}\left\{\begin{matrix}OC^2H^3O\\Cl\\OH\end{matrix}\right.\right)}_{\text{Aceto-hydrochloric glycerine.}}$$

*Action of Hypochlorous Acid.*—When hypochlorous acid acts on epichlorhydrin, the ether produced is a dichlorhydrin, not of glycerine, but of a tetratomic alcohol of the same series:

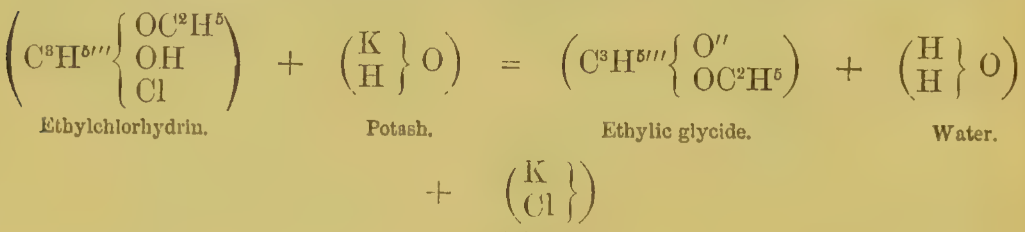
$$\underset{\text{Epichlorhydrin.}}{\left(C^3H^{5'''}\left\{\begin{matrix}O''\\Cl\end{matrix}\right.\right)} + \underset{\text{Hypochlorous acid.}}{\left(\left.\begin{matrix}Cl\\H\end{matrix}\right\}O\right)} = \underset{\text{Dichlorhydrin of propyl-phycite.}}{\left(C^3H^{4\text{iv}}\left\{\begin{matrix}Cl\\Cl\\OH\\OH\end{matrix}\right.\right)}$$

*Action of Alcohols.*—The different alcohols are also capable of uniting with epichlorhydrin or epibromhydrin, producing glyceric hydrochloro- or hydrobromo-alcoholic ethers:



$$\underset{\text{Epichlorhydrin.}}{\left(C^3H^{5'''}\left\{\begin{matrix}O''\\Cl\end{matrix}\right.\right)} + \underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)} = \underset{\text{Ethylchlorhydrin.}}{\left(C^3H^{5'''}\left\{\begin{matrix}OC^2H^5\\OH\\Cl\end{matrix}\right.\right)}$$

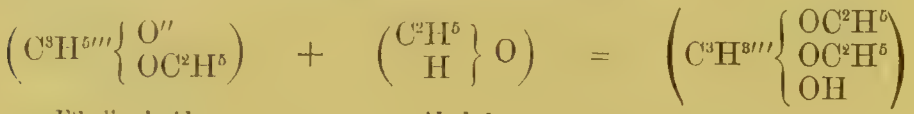
Treated by alkalies, these latter ethers lose a molecule of hydrochloric or hydrobromic acid and leave an alcoholic ether of glycide:



$$\underset{\text{Ethylchlorhydrin.}}{\left(C^3H^{5'''}\left\{\begin{matrix}OC^2H^5\\OH\\Cl\end{matrix}\right.\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Ethylic glycide.}}{\left(C^3H^{5'''}\left\{\begin{matrix}O''\\OC^2H^5\end{matrix}\right.\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

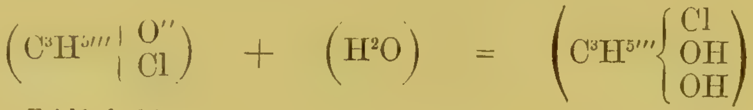
$$+ \underset{\text{Chloride of potassium.}}{\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)}$$

These new products can, in their turn, combine with the alcohols to form glyceric ethers which contain two radicles either of one monatomic alcohol or of two different monatomic alcohols:



$$\underset{\text{Ethylic glycide.}}{\left(C^3H^{5'''}\left\{\begin{matrix}O''\\OC^2H^5\end{matrix}\right.\right)} + \underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)} = \underset{\text{Diethyl-glycerine.}}{\left(C^3H^{5'''}\left\{\begin{matrix}OC^2H^5\\OC^2H^5\\OH\end{matrix}\right.\right)}$$

*Action of Water.*—Water is fixed directly by epichlorhydrin, and produces monohydrochloric glycerine:



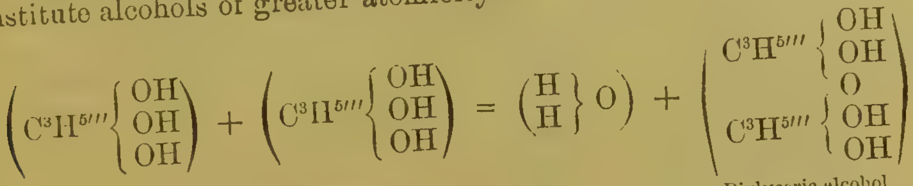
$$\underset{\text{Epichlorhydrin.}}{\left(C^3H^{5'''}\left\{\begin{matrix}O''\\Cl\end{matrix}\right.\right)} + \underset{\text{Water.}}{\left(H^2O\right)} = \underset{\text{Monochlorhydrin.}}{\left(C^3H^{5'''}\left\{\begin{matrix}Cl\\OH\\OH\end{matrix}\right.\right)}$$

On reviewing these preceding reactions, it will be seen that a first anhydride corresponds to glycerine, from which it differs by $(H^2O)$. While glycerine constitutes a triatomic alcohol, this first anhydride acts as a monatomic alcohol, of which all the derivatives have a tendency to return to the grouping of glycerine.

By the side of epichlorhydrin, M. Berthelot, and afterwards M. Reboul, have placed another body $(C^3H^4Cl^2)$, obtained by the action of potash on trichlorhydrin $(C^3H^5Cl^3)$. Though this body, which differs from trichlorhydrin by $(HCl)$, can return to its original state by combining with hydrochloric acid, it does not appear logical to regard it as belonging to the same grouping as glycerine.

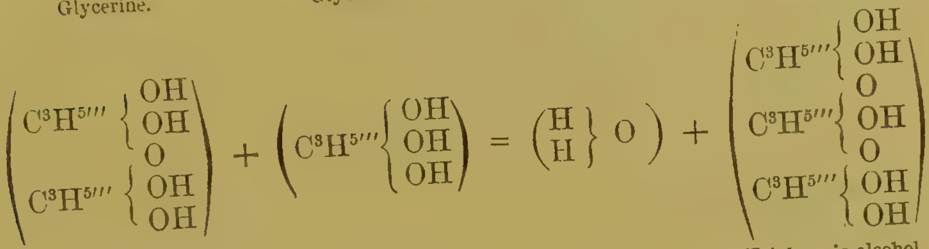
It is the same with the body M. Berthelot has described under the name of hemibromhydrin, and which is represented by the formula $(C^6H\,BrO^2)$.

Condensed Glycerines.—Two, three, . . . *n* atoms of glycerine may unite to form a single molecule, losing one, two, . . . $n-1$ molecules of water. The compounds which form contain a greater number of atoms of typical hydrogen than their generators, and consequently they constitute alcohols of greater atomicity :



$$\left(C^3H^{5'''}\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.\right) + \left(C^3H^{5'''}\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.\right) = \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + \left(\begin{matrix}C^3H^{5'''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\\O\\C^3H^{5'''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\end{matrix}\right)$$

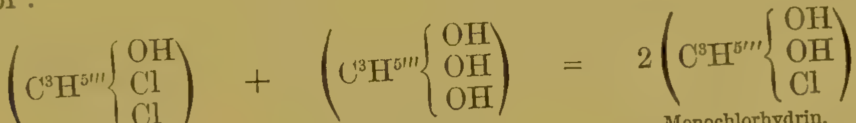
Glycerine. Glycerine. Water. Diglyceric alcohol.



$$\left(\begin{matrix}C^3H^{5'''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\\O\\C^3H^{5'''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\end{matrix}\right) + \left(C^3H^{5'''}\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.\right) = \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + \left(\begin{matrix}C^3H^{5'''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\\O\\C^3H^{5'''}\left\{\begin{matrix}OH\end{matrix}\right.\\O\\C^3H^{5'''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\end{matrix}\right)$$

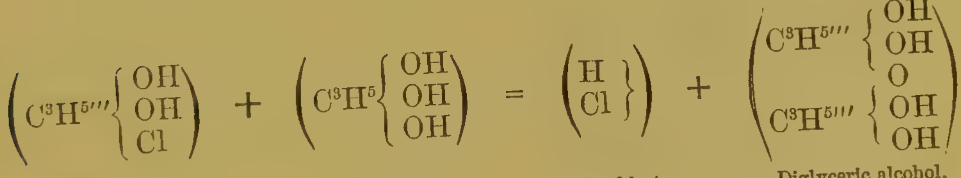
Diglyceric alcohol. Glycerine. Water. Triglyceric alcohol.

Mode of Preparation.—These bodies have only as yet been obtained by a single process, which consists in heating a mixture of mono- and di-chlorhydrin with glycerine. The dichlorhydrin is first transformed into monochlorhydrin, which, on reacting on glycerine, gives condensed alcohols. This reaction is identical with that which furnishes condensed glycols when the bromide of ethylene acts on glycol :



$$\left(C^3H^{5'''}\left\{\begin{matrix}OH\\Cl\\Cl\end{matrix}\right.\right) + \left(C^3H^{5'''}\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.\right) = 2\left(C^3H^{5'''}\left\{\begin{matrix}OH\\OH\\Cl\end{matrix}\right.\right)$$

Dichlorhydrin. Glycerine. Monochlorhydrin.



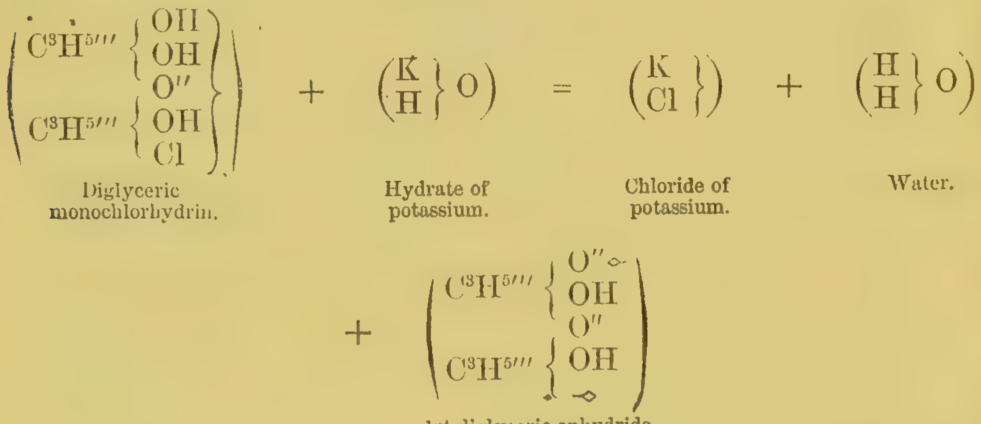
$$\left(C^3H^{5'''}\left\{\begin{matrix}OH\\OH\\Cl\end{matrix}\right.\right) + \left(C^3H^5\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.\right) = \left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right) + \left(\begin{matrix}C^3H^{5'''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\\O\\C^3H^{5'''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\end{matrix}\right)$$

Monochlorhydrin. Glycerine. Hydrochloric acid. Diglyceric alcohol.

The hydrochloric acid formed converts a fresh quantity of glycerine into monochlorhydrin, which, on contact with the diglyceric alcohol, produces triglyceric alcohol, and so on.

Polyglyceric alcohols ought to be separated from each other by fractional distillation in vacuo.

*Properties.*—The properties of the polyglyceric alcohols have been very little studied. It cannot, however, be doubted that they are true alcohols capable of being etherified. In fact, in the process used for their preparation, mono- and bi-hydrochloric ethers of diglyceric alcohol are also obtained. Under the influence of potash, monohydrochloric ether loses hydrochloric acid, and a first anhydride of diglyceric alcohol is produced :



$$\left(\begin{matrix} C^3H^{5'''}\left\{\begin{matrix}OH\\OH\end{matrix}\right. \\ O'' \\ C^3H^{5'''}\left\{\begin{matrix}OH\\Cl\end{matrix}\right.\end{matrix}\right) + \left(\begin{matrix}K\\H\end{matrix}\right\}O\Big) = \left(\begin{matrix}K\\Cl\end{matrix}\right\}\Big) + \left(\begin{matrix}H\\H\end{matrix}\right\}O\Big)$$

Diglyceric monochlorhydrin. Hydrate of potassium. Chloride of potassium. Water.

$$+ \left(\begin{matrix} C^3H^{5'''}\left\{\begin{matrix}O''\\OH\end{matrix}\right. \\ O'' \\ C^3H^{5'''}\left\{\begin{matrix}OH\\ \end{matrix}\right.\end{matrix}\right)$$

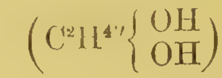
1st diglyceric anhydride.

It has already been seen that M. Berthelot's anomalous iodhydrin represents the monohydriodic ether of this anhydride acting as an alcohol. This iodhydrin, treated by potash, loses (HI) and leaves the oxide of glyceryl $\left(\begin{matrix}C^3H^{5'''}\\C^3H^{5'''}\end{matrix}\right\}O^3\Big)$, which may be regarded as the second diglyceric anhydride.

Thus while in the glycol series a single anhydride corresponds to each condensed glycol, the different condensed glycerines, being all biatomic, have several corresponding anhydrides.

It is a remarkable fact that in glycols, as in glycerines, the first anhydrides, derived either from the simple alcohol, or from the different products of condensation this forms, are polymers of each other.

**Glycols.**

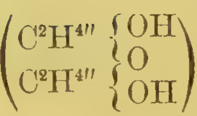


$$\left(C^2H^{4''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)$$

Glycol.

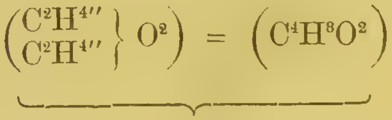
$(C^2H^4O)$

Anhydride of glycol.



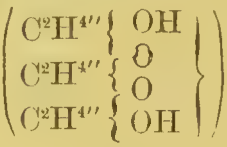
$$\left(\begin{matrix} C^2H^{4''}\left\{OH\right. \\ O \\ C^2H^{4''}\left\{OH\right.\end{matrix}\right)$$

Diethylenic glycol.



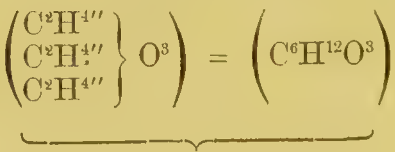
$$\underbrace{\left(\begin{matrix}C^2H^{4''}\\C^2H^{4''}\end{matrix}\right\}O^2\Big) = \left(C^4H^8O^2\right)}$$

Anhydride of diethylenic glycol.



$$\left(\begin{matrix} C^2H^{4''}\left\{OH\right. \\ O \\ C^2H^{4''} \\ O \\ C^2H^{4''}\left\{OH\right.\end{matrix}\right)$$

Triethylenic glycol.



$$\underbrace{\left(\begin{matrix}C^2H^{4''}\\C^2H^{4''}\\C^2H^{4''}\end{matrix}\right\}O^3\Big) = \left(C^6H^{12}O^3\right)}$$

Triethylenic anhydride.

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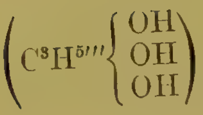
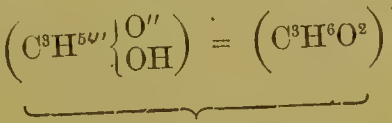
### Glycerines.



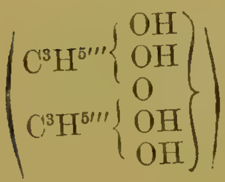
$$\left(C^3H^{5'''}\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.\right)$$

Glycerine.



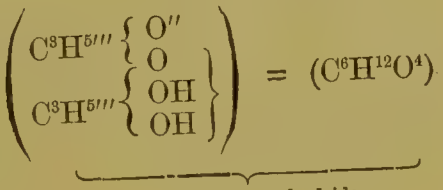
$$\underbrace{\left(C^3H^{5'''}\left\{\begin{matrix}O''\\OH\end{matrix}\right.\right) = \left(C^3H^6O^2\right)}$$

Glycide.



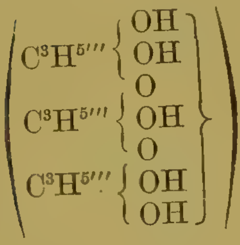
$$\left(\left.\begin{matrix}C^3H^{5'''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\\O\\C^3H^{5'''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\end{matrix}\right\}\right)$$

Diglyceric alcohol.



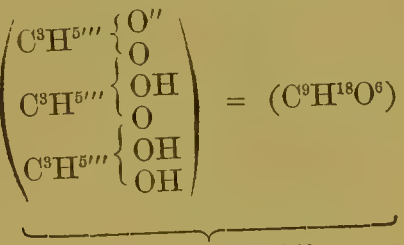
$$\underbrace{\left(\begin{matrix}C^3H^{5'''}\left\{\begin{matrix}O''\\O\end{matrix}\right.\\C^3H^{5'''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\end{matrix}\right) = \left(C^6H^{12}O^4\right)}$$

1st diglyceric anhydride.



$$\left(\left.\begin{matrix}C^3H^{5'''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\\O\\C^3H^{5'''}\left\{OH\right.\\O\\C^3H^{5'''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\end{matrix}\right\}\right)$$

Triglyceric alcohol.



$$\underbrace{\left(\begin{matrix}C^3H^{5'''}\left\{\begin{matrix}O''\\O\end{matrix}\right.\\C^3H^{5'''}\left\{\begin{matrix}OH\\O\end{matrix}\right.\\C^3H^{5'''}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\end{matrix}\right) = \left(C^9H^{18}O^6\right)}$$

1st triglyceric anhydride.

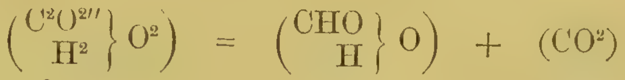
When speaking of phosphoric acid we have seen that this acid can give rise to condensed products, to each of which a first anhydride, polymer of the first phosphoric anhydride, corresponds. The discovery of the condensed glycols and glycerines first threw light on these mineral compounds, the comprehension of which was difficult, and whose real constitution could only be determined by analogy.

**Glyceric Compounds of Polybasic Acids.**—When glycerine is treated by a polybasic acid, the two bodies unite, eliminating water. The products formed belong to a more condensed type than each of their generators, and possess acid properties. They are products of condensation.

**Characters of ordinary Glycerine.**—Ordinary glycerine, when concentrated in vacuo, forms a thick, colourless, inodorous liquid of a sweet taste; it attracts the moisture of the atmosphere. Its density is 1·26 at 15°·5; it is soluble in water and alcohol in all proportions, and insoluble in ether. It dissolves the deliquescent salts, several metallic sulphates, chlorides, and nitrates, and the oxide of lead.

When left at a temperature of from 20° to 30° with water and malt yeast, glycerine undergoes a kind of fermentation in which propionic acid is produced, as well as a little acetic and formic acids, and a small quantity of gas.

When heated with oxalic acid dissolved in water, glycerine causes this body to split up into formic acid and carbonic anhydride, without taking part in the reaction except by its presence; the same quantity of glycerine serving indefinitely for the division of any quantity of oxalic acid :



$$\left(\left.\begin{matrix}C^2O^{2''}\\H^2\end{matrix}\right\}O^2\right) = \left(\left.\begin{matrix}CHO\\H\end{matrix}\right\}O\right) + (CO^2)$$

Oxalic acid. Formic acid. Carbonic anhydride.

## NOMENCLATURE OF ETHERS, GLYCOLS, AND GLYCERINE.

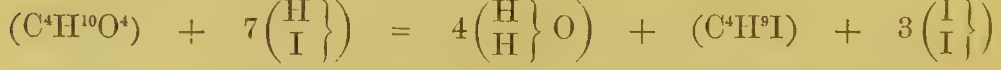
The nomenclature adopted for these ethers is very simple. The name glycol or glycerine is preceded by that of the acid of which the ether contains the radicle, the syllables *mono*, *di*, *tri*, being placed before this latter name, in order to indicate the degree of substitution. Sometimes the termination *ic* of the acid is replaced by *in*, and the name thus formed follows that of the alcohol. The generic name formed by means of the acid ought to be preceded by the syllables *mono*, *di*, *tri*, to indicate whether the ether is mono, di, or tri-acid. Thus we say diacetic glycol, or diacetin of glycol; trihydrochloric glycerine, or glyceric trichlorhydrin.

If several acid radicles enter into the constitution of an ether, a compound name should be formed from the two acids. Thus aceto-benzoate of glycol, glyceric hydrochloro-bromhydrin. When the ether contains an alcohol radicle, the name of this radicle is sometimes placed before that of the polyatomic alcohol, so as to unite these two names into one. For example, we may say glyceric diethylin, di-ethylic glycerine, or diethyl-glycerine.

## TETRATOMIC ALCOHOLS.

At present only two tetratomic alcohols are known. These are erythrite ($C^4H^{10}O^4$), and propylphycite ($C^3H^8O^4$). To these, perhaps, meconine ($C^{10}H^{10}O^4$) may hereafter be added.

*Erythrite* is derived from the fundamental hydrocarbide ($C^4H^{10}$), as are also butylic alcohol and butyl-glycol, from which it only differs by the quantity of oxygen it contains. Its true formula has been determined by M. de Luynes, who, by submitting it to the action of hydriodic acid, has transformed it into a compound which is an isomer of iodide of butyl ($C^4H^9I$), thereby showing that erythrite contains 4 atoms of carbon and 10 of hydrogen :



$$(C^4H^{10}O^4) + 7\left(\left.\begin{matrix}H\\I\end{matrix}\right\}\right) = 4\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + (C^4H^9I) + 3\left(\left.\begin{matrix}I\\I\end{matrix}\right\}\right)$$

Erythrite. Hydriodic acid. Water. Hydriodate of butylene. Iodine.

M. Berthelot has observed that erythrite combines directly with acids, eliminating water, like the alcohols; and he has given the name of erythrides to the ethers formed.

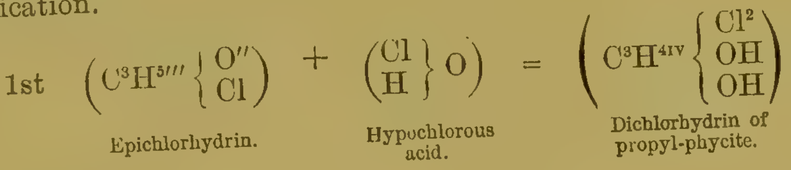
If it be considered that in all the series in which several alcohols of different atomicity are known, their oxygen increases in proportion to their atomicity, so that the atomicity is always equal to the number of atoms of oxygen, the atomicity of erythrite must be 4. Erythrite is therefore the tetratomic alcohol of a series already containing an alcohol and a glycol, but of which the glycerine is still wanting.

| $(C^4H^{10}O)$ | $(C^4H^{10}O^2)$ | $(C^4H^{10}O^3)$ | $(C^4H^{10}O^4)$ |
|---|---|---|---|
| Butylic alcohol. | Butyl-glycol. | Butyl-glycerine (unknown). | Erythrite. |

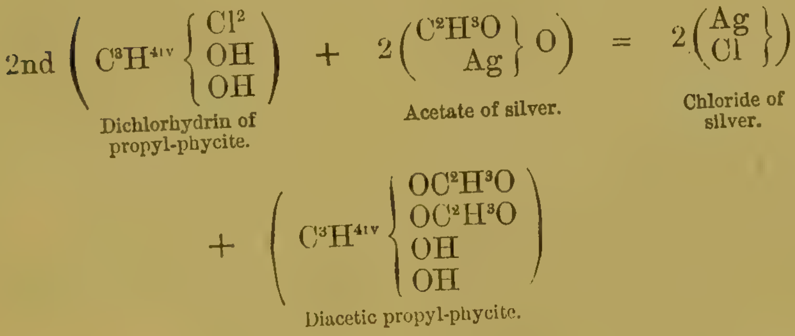
When submitted to the oxidizing action of platinum black, erythrite gives an acid which has not yet been studied.

*Propyl-phycite* has been obtained synthetically by M. Carius, who combined epichlorhydrin with hypochlorous acid, and thence obtained a dichlorhydrin of propyl-phycite.

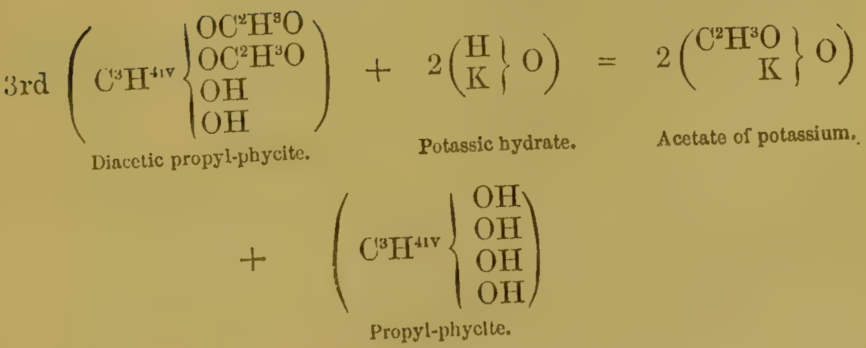
This dichlorhydrin, treated by acetate of silver, furnishes a diacetate of the same alcohol from which propyl-phycite has been prepared by saponification.



$$\text{1st}\quad \underset{\text{Epichlorhydrin.}}{\left(C^3H^{5'''}\left\{\begin{matrix}O''\\Cl\end{matrix}\right.\right)} + \underset{\text{Hypochlorous acid.}}{\left(\left.\begin{matrix}Cl\\H\end{matrix}\right\}O\right)} = \underset{\text{Dichlorhydrin of propyl-phycite.}}{\left(C^3H^{4iv}\left\{\begin{matrix}Cl^2\\OH\\OH\end{matrix}\right.\right)}$$



$$\text{2nd}\quad \underset{\text{Dichlorhydrin of propyl-phycite.}}{\left(C^3H^{4iv}\left\{\begin{matrix}Cl^2\\OH\\OH\end{matrix}\right.\right)} + \underset{\text{Acetate of silver.}}{2\left(\left.\begin{matrix}C^2H^3O\\Ag\end{matrix}\right\}O\right)} = \underset{\text{Chloride of silver.}}{2\left(\left.\begin{matrix}Ag\\Cl\end{matrix}\right\}\right)}$$
$$+ \underset{\text{Diacetic propyl-phycite.}}{\left(C^3H^{4iv}\left\{\begin{matrix}OC^2H^3O\\OC^2H^3O\\OH\\OH\end{matrix}\right.\right)}$$



$$\text{3rd}\quad \underset{\text{Diacetic propyl-phycite.}}{\left(C^3H^{4iv}\left\{\begin{matrix}OC^2H^3O\\OC^2H^3O\\OH\\OH\end{matrix}\right.\right)} + \underset{\text{Potassic hydrate.}}{2\left(\left.\begin{matrix}H\\K\end{matrix}\right\}O\right)} = \underset{\text{Acetate of potassium.}}{2\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right)}$$
$$+ \underset{\text{Propyl-phycite.}}{\left(C^3H^{4iv}\left\{\begin{matrix}OH\\OH\\OH\\OH\end{matrix}\right.\right)}$$

## PENTATOMIC ALCOHOLS.

No pentatomic alcohol is as yet known with certainty. But there exist two isomeric bodies, pinite and quercite, which may supply this deficiency. The formula of these two compounds is ($C^6H^{12}O^5$), and M. Berthelot has demonstrated that they act as alcohols. Considering that they contain 5 atoms of oxygen, they may be regarded as pentatomic alcohols.

Nevertheless, it must be observed that if our supposition be correct, pinite and quercite would constitute saturated or non-saturated alcohols, isologues of the unknown alcohol ($C^6H^{14}O^5$). If such an alcohol were submitted to the action of oxidants, it ought to furnish a first aldehyd ($C^6H^{12}O^5$).

Moreover, alcohols may give rise to a number of aldehyds equal to the number of their atomicity; and the last, the least hydrogenized of these aldehyds, alone ought to have entirely lost the characteristics of an alcohol. The others probably have both alcoholic and aldehydic properties; the first of these properties predominating in the first products of oxidation, the latter properties in the last.

If therefore the first aldehyd ($C^6H^{12}O^5$) of the unknown pentatomic alcohol ($C^6H^{14}O^5$) were obtained, it would act as a tetratomic alcohol.

Is pinite the first aldehyd of the unknown alcohol ($C^6H^{14}O^5$), or is it an alcohol isologous with the first? It is impossible to decide this question. Nevertheless, if pinite and quercite are non-saturated bodies, they might be transformed into the unknown alcohol ($C^6H^{14}O^5$) by the action of nascent hydrogen. It would then be seen whether this alcohol re-formed the body by oxidation or not. If the regeneration took place, the aldehydic nature of pinite and quercite would be decided; if not, these bodies might be regarded simply as pentatomic alcohols: an alcohol always gives aldehyds by oxidation, but never other alcohols isologous with the first.

## HEXATOMIC ALCOHOLS.

Two isomeric bodies are known, mannite and dulcite ($C^6H^{14}O^6$), which act as saturated hexatomic alcohols and give rise to two parallel series of compounds. Besides these, several isomeric bodies are known corresponding to the formula ($C^6H^{12}O^6$), which appear to act as hexatomic alcohols, or perhaps as aldehyds of the first degree, derived from saturated hexatomic alcohols by the loss of $H^2$. They are the glucoses.

## SATURATED HEXATOMIC ALCOHOLS.

Preparation.—These bodies have not been prepared synthetically. They are extracted from vegetable products, and one of them, mannite, is formed when glucose is submitted to the action of nascent hydrogen.

Properties.—1st. *Action of Heat.*—Under the influence of heat, these alcohols lose a molecule of water, and are transformed into a first anhydride, of a syrupy consistence:

$$\underset{\text{Dulcite.}}{(C^6H^{14}O^6)} = \underset{\text{Water.}}{(H^2O)} + \underset{\text{Dulcitane.}}{(C^6H^{12}O^5)}$$

2nd. *Action of Oxidants.*—Powerful oxidants destroy the molecule of these bodies and cause the formation of oxalic acid. When they are less active they give rise to acids, which are derived from these alcohols by the substitution of one or more atoms of oxygen for two atoms of hydrogen or a multiple of two of these atoms. Under the influence of platinum black, the aqueous solution of mannite has been transformed into mannitic acid, the formula of which is $(C^6H^{12}O^7)$, and into a saccharine compound, mannitose, corresponding to the formula $(C^6H^{12}O^6)$.

Dilute nitric acid converts mannite into an acid which appears to be analogous or identical with saccharic acid $(C^6H^{16}O^8)$, and it converts dulcite into an isomer of this acid, mucic acid.

$$2\underset{\text{Mannite.}}{\left(C^6H^{14}O^6\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} = 2\underset{\text{Mannitose.}}{\left(C^6H^{12}O^6\right)} + 2\underset{\text{Water.}}{\left(H^2O\right)}$$

$$\underset{\text{Mannite.}}{\left(C^6H^{14}O^6\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} = \underset{\text{Mannitic acid.}}{\left(C^6H^{12}O^7\right)} + \underset{\text{Water.}}{\left(H^2O\right)}$$

$$\underset{\text{Mannite.}}{\left(C^6H^{14}O^6\right)} + 2\underset{\text{Oxygen.}}{\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\right)} = \underset{\text{Saccharic acid.}}{\left(C^6H^{10}O^8\right)} + 2\underset{\text{Water.}}{\left(H^2O\right)}$$

$$\underset{\text{Dulcite.}}{\left(C^6H^{14}O^6\right)} + 2\underset{\text{Oxygen.}}{\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\right)} = \underset{\text{Mucic acid.}}{\left(C^6H^{10}O^8\right)} + 2\underset{\text{Water.}}{\left(H^2O\right)}$$

The transformation of mannite into mannitic and saccharic acids, and that of dulcite into mucic acid, is entirely analogous to the transformation of glycol into glycolic and oxalic acids.

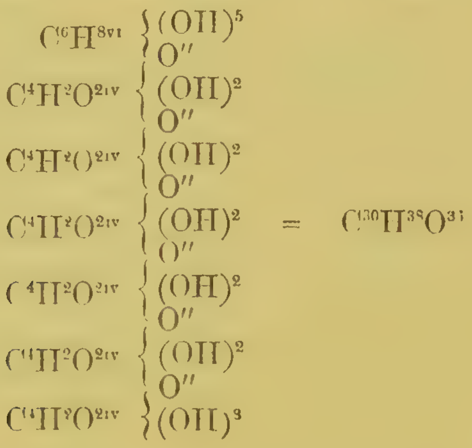
3rd. *Action of Monatomic Acids.*—At 100° these alcohols do not absorb gaseous hydrochloric acid, but if the acid be in concentrated aqueous solution, they combine with it, eliminating water and giving rise to a neutral compound.

With acetic, butyric, valeric, benzoic, and other acids, at a temperature of 250°, neutral compounds are also produced with elimination of water.

These different compounds are analogous to the simple and compound ethers of the other alcohols, and particularly of glycerine. M. Berthelot calls these bodies mannitanides or dulcitanides, according as they are derived from mannite or dulcite.

Monohydrated nitric acid converts mannite into hexanitric mannite $\left(\left.\begin{matrix}C^6H^{8\text{vi}}\\(NO^2)^6\end{matrix}\right\}O^6\right)$.

4th. *Action of Polybasic Acids.*—Polybasic acids act on these alcohols in the same manner as on glycerine or glycols, that is to say, they produce condensed compounds which possess acid properties. Thus with mannite and tartaric acid mannitartaric acid is obtained.



$$\begin{array}{ll} C^6H^{8\text{vi}} & \left\{\begin{matrix}(OH)^5\\O''\end{matrix}\right. \\ C^4H^2O^{2\text{iv}} & \left\{\begin{matrix}(OH)^2\\O''\end{matrix}\right. \\ C^4H^2O^{2\text{iv}} & \left\{\begin{matrix}(OH)^2\\O''\end{matrix}\right. \\ C^4H^2O^{2\text{iv}} & \left\{\begin{matrix}(OH)^2\\O''\end{matrix}\right. \quad = \quad C^{30}H^{38}O^{31} \\ C^4H^2O^{2\text{iv}} & \left\{\begin{matrix}(OH)^2\\O''\end{matrix}\right. \\ C^4H^2O^{2\text{iv}} & \left\{\begin{matrix}(OH)^2\\O''\end{matrix}\right. \\ C^4H^2O^{2\text{iv}} & \left\{(OH)^3\right. \end{array}$$

5th. *Action of Hydriodic Acid.*—Hydriodic acid with the aid of heat transforms mannite into hydriodate of hexylene, producing water and a deposit of iodine:

$$\underset{\text{Mannite.}}{\left(C^6H^{14}O^6\right)} + \underset{\text{Hydriodic acid.}}{11\left(\left.\begin{matrix}H\\I\end{matrix}\right\}\right)} = \underset{\text{Hydriodate of hexylene.}}{\left(C^6H^{13}I\right)} + \underset{\text{Iodine.}}{5\left(\left.\begin{matrix}I\\I\end{matrix}\right\}\right)} + \underset{\text{Water.}}{6\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

This reaction, discovered by MM. Wanklyn and Erlenmeyer, has definitely established the formula of mannite.

6th. *Action of Alcohols.*—Monatomic alcohols do not act directly on mannite and dulcite, but if their hydrobromic ether be heated in a hermetically-sealed tube with mannite, water, and potash, an alcoholic ether of mannite is produced. It is thus that M. Berthelot has prepared the compound $\left(\left.\begin{matrix}C^6H^{8\text{vi}}\\(C^2H^5)^2\\H^2\end{matrix}\right\}O^5\right)$, which he derives from mannitane.

7th. *Action of Bases.*—Bases combine in all proportions with mannite and dulcite, as with the other alcohols.

**Saponification of Mannitanides and Dulcitanides.**—These ethers, when treated with bases, do not re-form the hexatomic radicle from which they are derived, but its first anhydride. Mannitanides give mannitane ($C^6H^{12}O^5$), and dulcitanides give dulcitane. In an experiment on butyric mannite, M. Berthelot has obtained a second mannitic anhydride, which he calls mannide.

Heated with acids, mannitane and dulcitane re-form the original mannitanides and dulcitanides. It appears to be the same with mannide.

Remarks on the foregoing Facts.—From the fact of the production of mannitane by the saponification of mannitanides, and the production of mannitanides by means of mannitane, M. Berthelot concludes that mannite is not an alcohol; that the alcoholic properties are contained in mannitane; and he assigns to this latter body an atomicity equal to six.

We cannot accept this view. It cannot be doubted that mannitane is an alcohol, as we have seen that the alcoholic anhydrides retain the functions of the bodies whence they are derived, when they still contain typical hydrogen. But the true and fundamental alcohol is mannite; it has an atomicity equal to 6, as is demonstrated by its six atoms of oxygen, as well as by the fact of the possible substitution of six times the group ($NO^2$) for 6H in hexanitric mannite.

Mannitane is only an anhydride, which possesses two atoms of typical hydrogen less than its generator, and which ought to act as a tetratomic alcohol.

This theory accounts for the facts as well as that of M. Berthelot, and it has moreover the great advantage of not disagreeing with the laws observed in the other alcoholic series.

The study of condensed alcohols has shown that, in proportion as the molecules become complicated, the fundamental compounds have less stability, and anhydrides have greater tendency to be produced. Thus ordinary glycol has such stability that it is obtained by the action of oxide of ethylene on water. Decyl-glycol, on the contrary, is so unstable that in the saponification of its ethers it decomposes, and simply furnishes an anhydride.

Applying these remarks to mannite, the facts become developed with great clearness. When mannite is heated with an acid, a hexatomic ether is produced. If this ether be saponified, the mannite group not having sufficient stability to resist the molecular shock, only an anhydride of this alcohol, mannitane or mannide, is obtained.

If this anhydride be heated with an acid, it is first saturated, uniting with a number of molecules of the hydrated acid equivalent to the number of molecules of water by which it differs from mannite. Mannitane therefore unites to one, and mannide to two acid molecules. This first reaction gives rise, according to the anhydride employed, to a mono- or bi-acid ether of mannite; it is analogous to that produced when oxide of ethylene or epichlorhydrin is submitted to the action of acids.

Mannitic ether when formed may, by an ulterior etherifying action, be transformed into mannite containing two, three, . . . six acid residues.

The only objection M. Berthelot can oppose to this interpretation of the facts is that, on analyzing the compounds of which we speak, they do not answer to the formula of a hexacid mannite, but, on the contrary, they answer to that of a hexacid ether of mannitane.

M. Berthelot seeks to establish that, between the composition of a hexacid ether of mannite and of a hexacid ether of mannitane, there is a greater difference than could result from a mere error of analysis. This fact would be conclusive if we could be perfectly sure of the purity of the product analyzed. But as, after all, mannitane can act as a tetratomic alcohol, inasmuch as it contains four atoms of typical hydrogen, there may also be mixtures of mannitic and mannitanic ethers which analysis is unable to determine; and it is probable that when mannite is heated to 200° with an acid, the portion of this sugar which does not enter into reaction is transformed into mannitane, and that this anhydride combines with the mannitic ether already produced, forming condensed compounds which again serve to increase the confusion. It is still more probable that such a phenomenon is produced when mannitane is directly heated with an acid.

To sum up, we regard mannite as a hexatomic alcohol, and mannitane as an anhydride which can act as a tetratomic alcohol, but which has a greater tendency to combine with acids without eliminating water to re-form a monacid ether of the alcohol whence it was formed.

The oxidation of mannite serves to support our interpretation. If it be mannitane that acts as alcohol, the first acid of this alcohol would have $(C^6H^{10}O^6)$ for formula, and the second $(C^6H^8O^7)$, as the two following equations indicate:

$$\underset{\text{Mannitane.}}{(C^6H^{12}O^5)} + \underset{\text{Oxygen.}}{O^2} = \underset{\text{Water.}}{(H^2O)} + \underset{\text{1st acid.}}{(C^6H^{10}O^6)}$$

$$\underset{\text{Mannitane.}}{(C^6H^{12}O^5)} + \underset{\text{Oxygen.}}{O^4} = \underset{\text{Water.}}{2(H^2O)} + \underset{\text{2nd acid.}}{(C^6H^8O^7)}$$

If, on the contrary, it be mannite which acts as alcohol, the two first acids which would be derived by oxidation would have for formulæ $(C^6H^{12}O^7)$ and $(C^6H^{10}O^8)$, as the following equations show:

$$\underset{\text{Mannite.}}{(C^6H^{14}O^6)} + \underset{\text{Oxygen.}}{O^2} = \underset{\text{Water.}}{(H^2O)} + \underset{\text{1st acid.}}{(C^6H^{12}O^7)}$$

$$\underset{\text{Mannite.}}{(C^6H^{14}O^6)} + \underset{\text{Oxygen.}}{O^4} = \underset{\text{Water.}}{2(H^2O)} + \underset{\text{2nd acid.}}{(C^6H^{10}O^8)}$$

The acid $(C^6H^{12}O^7)$ is none other than the mannitic acid obtained by M. Gorup Besanez by oxidizing mannite by platinum black, and the acid $(C^6H^{10}O^8)$ is the saccharic acid which is obtained when mannite is oxidized by nitric acid.

## GLUCOSES.

Besides mannite and dulcite, we have said that there exists a class of isomeric bodies known under the name of glucoses, and corresponding to the formula $(C^6H^{12}O^6)$. These bodies can combine with acids like mannite, but what is their atomicity? Are they hexatomic alcohols sologues of mannite as their six atoms of oxygen appear to indicate? Are they not rather aldehyds derived from mannite and dulcite, and cting as alcohols with an atomicity of 5?

M. Berthelot asks these two questions without solving them, but ve believe that a solution may be arrived at.

M. Linnemann has discovered that ordinary glucose absorbs nascent hydrogen, and is transformed into mannite. This body cannot thereore be considered as a hexatomic alcohol derived from a saturated hydrocarbide ($C^6H^{12}$). But we have seen that a non-saturated hydrocarbide can give derivatives of the same degree of saturation as itself. Hence glucose may be a non-saturated alcohol as well as an aldehyd, and Linnemann's experiment throws no light on this point.

But as yet we know no instance of an alcohol which, on oxidizing, loses hydrogen and gives rise to a new alcohol isologous with the first. In this case it is always an aldehyd which is formed. M. Gorup Besanez has obtained a glucose by the oxidation of mannite, and this reaction gives great weight to the opinion that glucoses are aldehyds of the first degree.

The following is another proof: glucose is transformed into saccharic acid by oxidants, and this oxidation can only be explained by admitting that this body is an aldehyd, when we can understand that it can fix an atom of oxygen before undergoing a new substitution.

In relation to the question whether they be glucoses or their first anhydrides, the glucosanes ($C^6H^{10}O^5$), which act as alcohols, we might repeat what we said when speaking of mannite. Besides, here we approach M. Berthelot's opinions, who admits that there may be ethers both of the glucoses and of the glucosanes. To sum up, we consider the glucoses as acting the part of aldehyds of the first degree and of pentatomic alcohols, and as being capable of producing anhydrides—glucosanes, which retain the functions of the bodies whence they are derived. The glucoses known are very numerous. They are:

1st. Ordinary glucose, which is produced by the hydration of starch under the influence of dilute acids or of diastase (the ferment which exists in malt); this glucose is also found in honey, inverted sugar, and grape sugar; it constitutes the saccharine principle of diabetic urine.

2nd. Maltose, which only differs from glucose in its rotatory action on light, and which is obtained by the incomplete germination of barley.

3rd. Levulose, which exists in cane sugar inverted by acids, and which is obtained in a pure state by hydrating inulin, a compound analogous to starch, by means of dilute acids.

4th. Mannitose, obtained by the oxidation of mannite.

5th. Galactose, which is prepared by causing acids to act on lactose or sugar of milk.

6th. Inosite, which is extracted from the muscular tissue.

7th. Sorbin, extracted from the juice of the berries of the service-tree (*Sorbus aucuparia*).

8th. Eucalyn, which is produced in the fermentation of melitose in consequence of the destruction of another saccharine principle which, united with eucalyn, appears to constitute melitose.

The first four of these glucoses present great analogies to one another; they scarcely differ except in their rotatory action on light, in certain physical properties, and some chemical properties of slight importance. They are four allotropic states of the same body rather than four isomers.

Galactose differs more from the preceding bodies. While these furnish saccharic acid by oxidation, galactose furnishes an acid isomeric with this, mucic acid ($C^6H^{10}O^8$).

The last three glucoses in the list differ by more marked properties. While all the others can undergo alcoholic fermentation under the influence of yeast of beer, these do not ferment at all, or only under special conditions. With the exception of inosite, the glucoses are decomposed at 100° under the influence of alkalies; they reduce cupro-potassic tartrate with precipitation of red sub-oxide of copper; and they are not charred by cold concentrated sulphuric acid. They are clearly to be distinguished from mannite and dulcite, which are not decomposed under the influence of alkalies at 100°.

The ethers of the glucoses are called glucosides.

A great number of glucosides exist in vegetables; they are amygdalin, arbutin, phillyrin, salicin, esculin, populin, etc. Under the influence of hydrating agents, all these bodies are capable of absorbing the elements of water, and of being split up into glucose and a number of other products, among which are acids, aldehyds, ammonias, and phenols. We cannot dilate on these substances; but one fact must be noticed which is observed in the saponification of populin.

The formula of populin is ($C^{20}H^{22}O^8$); it is a benzoico-saligenic glucoside, the rational formula of which may be written $\left(\left.\begin{matrix} C^6H^{6vi} \\ C^7H^7O' \\ C^7H^5O' \\ H^4 \end{matrix}\right\} O^6\right)$.

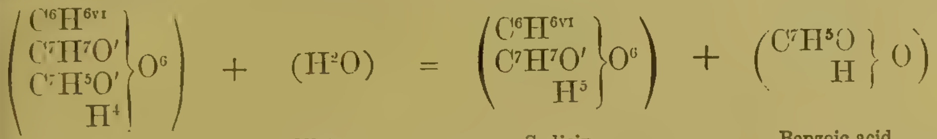
($C^6H^6$) is the hexatomic radicle of glucose ($C^7H^7O$), the monatomic residue which is derived from saligenin ($C^7H^8O^2$) by the elimination of the group (HO), and ($C^7H^5O$) is the monatomic radicle of benzoic acid.

On taking up the elements of water, populin ought therefore to be transformed into glucose saligenin and benzoic acid:

$$\underset{\text{Populin.}}{\left(\left.\begin{matrix} C^6H^{6vi} \\ C^7H^7O' \\ C^7H^5O' \\ H^4 \end{matrix}\right\} O^6\right)} + \underset{\text{Water.}}{2\,(H^2O)} = \underset{\text{Glucose.}}{\left(\left.\begin{matrix} C^6H^{6vi} \\ H^6 \end{matrix}\right\} O^6\right)} + \underset{\text{Saligenin.}}{(C^7H^8O^2)}$$

$$+ \underset{\text{Benzoic acid.}}{\left(\left.\begin{matrix} C^7H^5O \\ H \end{matrix}\right\} O\right)}$$

However, if these actions be carefully managed, this complete livision does not take place all at once, benzoic acid and salicin are irst obtained:



$$\left(\left.\begin{array}{r}C^{16}H^{6vi}\\C^{7}H^{7}O'\\C^{7}H^{5}O'\\H^{4}\end{array}\right\}O^{6}\right) + (H^{2}O) = \left(\left.\begin{array}{r}C^{16}H^{6vi}\\C^{7}H^{7}O'\\H^{5}\end{array}\right\}O^{6}\right) + \left(\left.\begin{array}{r}C^{7}H^{5}O\\H\end{array}\right\}O\right)$$

Populin. Water. Salicin. Benzoic acid.

It is only by an ulterior action that salicin is transformed into aligenin and glucose.

It will be seen from this that in the saponification of the glucosides, if he reaction be well chosen and managed, the different products which nter into the composition of these bodies may be extracted one by ne.

### STUDY OF THE PRINCIPAL SATURATED HEXATOMIC ALCOHOLS.

**Mannite** ($C^6H^{14}O^6$).—Mannite was discovered by Proust, and its composition determined by Liebig. It exists in a great number of vegetables, and in the saccharine juices which have undergone viscous or lactic fermentation; it is generally extracted from manna, by digesting this substance with boiling alcohol, filtering while hot, and crystallizing; it should be purified by repeated crystallizations.

Recently, M. Linnemann has prepared mannite from inverted sugar. To effect this he inverts a certain quantity of cane sugar by sulphuric acid, he then saturates the liquid with a slight excess of alkali, and adds sodium amalgam. As the reaction develops a considerable amount of heat the liquid must be cooled; when the action is completed, the liquid is saturated with sulphuric acid, evaporated to dryness, and the mannite is extracted from the residue by means of alcohol, as in extracting mannite from manna.

Mannite is a solid substance, fusible between 160° and 165°, and when once melted it can remain liquid at 140°. It exercises no action on polarized light; it dissolves in six and a half times its weight of water at 18°, and in 80 parts of cold alcohol of the strength of 89 per cent., and much more readily at the boiling temperature. Absolute alcohol only dissolves fourteen per cent. of its weight of mannite; ether does not dissolve it at all.

Mannite is deposited from its alcoholic solution in thin, colourless, quadrangular, silky prisms. Its aqueous solution, when mixed with sulphate of copper, prevents the precipitation of this latter by potash. The alkaline liquor, when boiled, does not deposit sub-oxide of copper. Fehling's liquor also resists the action of mannite.

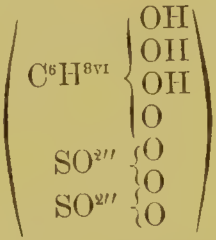
If mannite be raised to the temperature of about 200°, ebullition takes place, the greater part of this sugar remains almost unaltered, and scarcely coloured; another part is dehydrated and transformed into mannitane, according to the equation:

$$(C^6H^{14}O^6) = (H^2O) + (C^6H^{12}O^5)$$

Mannite. Water. Mannitane.

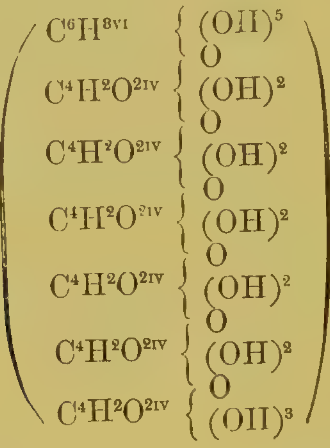
Above 300° mannite is destroyed, leaving a porous charcoal. If, instead of calcining it alone, it be mixed with eight times its weight of lime, metacetone is obtained: calcined with potash—formiate, acetate, and propionate of potassium are formed.

Mannite is not charred by sulphuric acid, either when cold or hot. If the product resulting from the reaction be saturated with carbonate of barium, a salt of sulphomannitic acid is obtained in solution. This acid answers to the formula:



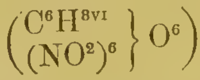
$$\left(\begin{array}{ll} C^6H^{8vi} & \left\{\begin{array}{l} OH \\ OH \\ OH \\ O \end{array}\right. \\ SO^{2''} & \left\{\begin{array}{l} O \\ O \end{array}\right. \\ SO^{2''} & \left\{\begin{array}{l} O \end{array}\right. \end{array}\right)$$

At 100° mannite does not absorb gaseous hydrochloric acid, but combines with it, eliminating water, and gives rise to a neutral compound if the acid be in concentrated aqueous solution. With acetic, butyric, valeric, benzoic, and other acids, at a temperature of 250°, neutral compounds are produced analogous to the compound ethers and fats. M. Berthelot calls them *mannitanides*. To isolate these compounds the excess of acid is saturated by an alkali, and they are treated with ether, which dissolves the compound formed. With mannite, tartaric acid forms an acid which has received the name of *mannitartaric acid*, and of which the formula is:



$$\left(\begin{array}{ll} C^6H^{8vi} & \left\{\begin{array}{l} (OH)^5 \\ O \end{array}\right. \\ C^4H^2O^{2iv} & \left\{\begin{array}{l} (OH)^2 \\ O \end{array}\right. \\ C^4H^2O^{2iv} & \left\{\begin{array}{l} (OH)^2 \\ O \end{array}\right. \\ C^4H^2O^{2iv} & \left\{\begin{array}{l} (OH)^2 \\ O \end{array}\right. \\ C^4H^2O^{2iv} & \left\{\begin{array}{l} (OH)^2 \\ O \end{array}\right. \\ C^4H^2O^{2iv} & \left\{\begin{array}{l} (OH)^2 \\ O \end{array}\right. \\ C^4H^2O^{2iv} & \left\{\begin{array}{l} (OH)^3 \end{array}\right. \end{array}\right)$$

With monohydrated nitric acid hexanitric mannite is obtained:



$$\left(\left.\begin{array}{l} C^6H^{8vi} \\ (NO^2)^6 \end{array}\right\} O^6\right)$$

Oxalic acid is decomposed into formic acid and carbonic anhydride by the simple presence of mannite, exactly as by glycerine. On heating a mixture of mannite, potash in concentrated aqueous solution, and bromide of ethyl for about forty hours in a water bath, then treating with ether, and evaporating this liquid, ethyl-mannite ($C^{10}H^{20}O^5$) is obtained, which may be written $\left(\left.\begin{matrix}C^6H^{8\mathrm{vi}}\\(C^2H^5)^2\\H^2\end{matrix}\right\}O^5\right)$, deriving it from mannitane $\left(\left.\begin{matrix}C^6H^{8\mathrm{vi}}\\H^4\end{matrix}\right\}O^5\right)$.

Bases readily combine with mannite. These combinations are obtained by dissolving the base in a solution of mannite and precipitating by alcohol. Two calcic compounds are known, which have the formulæ:

$$(CaO, C^6H^{14}O^6 + 2aq.) \text{ and } (CaO, (C^6H^{14}O^6)^2).$$

Baryta only furnishes a single compound, the formula of which is $((BaO)^2, C^6H^{14}O^6)$; with strontia also only a single compound, which has the formula ($StO, C^6H^{14}O^6$), has been obtained. The ammoniacal acetate of lead precipitates mannite, and the formula of the precipitate is ($C^6H^{10}Pb^2O^6$). When mannite is submitted to the action of oxidants, the effects vary according to the activity of the agents employed: if these be very active, oxalic acid is produced; if they are less so, as in the case of very dilute nitric acid, an acid is produced which appears to be identical with saccharic acid, and if platinum black be made to act on a concentrated solution of mannite, it gives rise to an acid which has received the name of *mannitic acid*, and at the same time to an inactive sugar of the glucose family which is called *mannitose*. Mannitic acid is derived from mannite by a reaction analogous to that in which acetic, glycolic, and glyceric acids are respectively derived from alcohol, glycol, and glycerine.

$$\underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)} + \underset{\text{Oxygen.}}{O^2} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Acetic acid.}}{\left(\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O\right)}$$

$$\underset{\text{Glycol.}}{\left(\left.\begin{matrix}C^2H^{4''}\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Oxygen.}}{O^2} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Glycolic acid.}}{\left(\left.\begin{matrix}C^2H^2O''\\H^2\end{matrix}\right\}O^2\right)}$$

$$\underset{\text{Glycerine.}}{\left(\left.\begin{matrix}C^3H^{5'''}\\H^3\end{matrix}\right\}O^3\right)} + \underset{\text{Oxygen.}}{O^2} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Glyceric acid.}}{\left(\left.\begin{matrix}C^3H^3O'''\\H^3\end{matrix}\right\}O^3\right)}$$

$$\underset{\text{Mannite.}}{\left(\left.\begin{matrix}C^6H^{8\mathrm{vi}}\\H^6\end{matrix}\right\}O^6\right)} + \underset{\text{Oxygen.}}{O^2} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Mannitic acid.}}{\left(\left.\begin{matrix}C^6H^6O^{\mathrm{vi}}\\H^6\end{matrix}\right\}O^6\right)}$$

Distilled in a current of carbonic anhydride in presence of a highly-concentrated solution of hydriodic acid, mannite is transformed into iodide of hexyl ($C^6H^{13}I$) according to the equation:

$$\underset{\text{Mannite.}}{(C^6H^{14}O^6)} + \underset{\text{Hydriodic acid.}}{11\left(\left.\begin{matrix}H\\I\end{matrix}\right\}\right)} = \underset{\text{Water.}}{6\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Iodide of hexyl.}}{\left(\left.\begin{matrix}C^6H^{13}\\I\end{matrix}\right\}\right)} + \underset{\text{Iodine.}}{5\left(\left.\begin{matrix}I\\I\end{matrix}\right\}\right)}$$

This reaction, which is entirely identical with that which transforms glycerine into iodide of propyl, definitely fixes the composition of mannite, and renders the formula ($C^3H^7O^3$), which some chemists have given to it, quite inadmissible.

In presence of yeast of beer, mannite does not ferment; if its solution be maintained at 40°, after having been mixed with chalk and poor cheese, pancreatic tissue or albumen, fermentation takes place, hydrogen and carbonic anhydride are disengaged, and alcohol is produced along with lactic and butyric acids. These two acids appear to be the result of a concomitant fermentation, but different from that which furnishes alcohol. M. Berthelot affirms that in this latter fermentation no yeast is formed.

MANNITANE ($C^6H^{12}O^5$).—Mannitane, or the first anhydride of mannite, can, according to Berthelot, be obtained by three processes, which are: 1st, the saponification of mannitic ethers; 2nd, the action of a temperature of 200° on mannite; 3rd, the action of hydrochloric acid at a temperature of 100° on mannite.

In order to saponify mannitic ethers, they may either be heated with water to 240°, or with an alkaline solution to 100°, or again they may be dissolved in alcohol and hydrochloric acid added. In this case the alcohol seizes the acid of mannitic ether and the mannitane is set free. Whichever method be used to prepare it, mannitane must be purified by several successive solutions in absolute alcohol, which dissolves none of the impurities.

The formula of mannitane is ($C^6H^{12}O^5$); it is a syrupy liquid; it gives off vapours at 140°; on contact with air it absorbs moisture and re-forms crystals of mannite; this regeneration takes place with much greater rapidity if mannitane be heated in a sealed tube with solution of baryta.

Mannitane, when heated with acids in sealed tubes, forms the same neutral compounds as mannite.

From the two facts that mannitanides produce mannitane when they are saponified, and that they are re-formed by means of mannitane and acids, M. Berthelot concludes that it is not mannite, but mannitane, which is an alcohol, and that mannite is only a hydrate of this alcohol. He supports his view by the number of mannitanides which the same monobasic acid can furnish with mannitane, and considers this body as an hexatomic alcohol: we have already considered this question.

MANNIDE ($C^6H^{10}O^4$).—Mannide, or the second anhydride of mannite, has been obtained by Berthelot as a secondary product in the preparation of butyric mannite.

It is a syrupy substance; its taste is sweetish at first, afterwards bitter, and it is soluble in water and alcohol.

Mannide furnishes mannite under the same conditions as mannitane: heated with benzoic acid it gives rise to a neutral compound which is soluble in ether, and which appears to be benzoic mannite. The dehydration of mannite has not been pursued further than mannide.

**Dulcite** ($C^6H^{14}O^6$) (synonyms: *Dulcose, Dulcin*).—In 1848, there came from Madagascar a substance in small roots covered with crystals, and the botanic origin of which was unknown. From this substance, Laurent extracted dulcite by simply digesting it in boiling water, filtering, and leaving the filtered liquor to cool.

Since then, M. Eichler has given a process for the extraction from *Melampyrum nemorosum* of a substance which he calls melampyrin, and which Gilmer has shown to be identical with Laurent's dulcite.

In order to extract dulcite from *Melampyrum nemorosum*, a decoction of this herb is made; sufficient lime is added to render the liquid alkaline, and it is then concentrated; the lime is saturated with hydrochloric acid in slight excess; the liquid is somewhat further evaporated, and on allowing it to cool, dulcite is obtained in very white crystals.

Dulcite has a sweet taste, similar to that of mannite; it dissolves readily in water, but with difficulty in alcohol; it fuses at 182°, and is destroyed at 275°, becoming charred.

Dulcite crystallizes in oblique rhombohedric prisms; it produces no rotation on polarized light; boiling alkalies do not affect it; acids act with it as with mannite. When treated by nitric acid, it is converted into oxalic and mucic acids. According to M. Carlet, a certain quantity of paratartaric acid is also produced. This latter fact appears to indicate that it is only inactive on polarized light by compensation.

With lime and baryta, dulcite gives compounds which are analogous to those furnished by mannite; it is also precipitated by ammoniacal acetate of lead.

In presence of yeast of beer, dulcite does not ferment. If it be mixed with chalk, poor cheese and water, and the mixture be kept at 40°, hydrogen, carbonic anhydride, alcohol, butyric acid, and lactic acid, are produced.

Under the influence of heat, dulcite loses a molecule of water and gives dulcitane, which is isolated by dissolving it in alcohol; moreover, dulcitane may be obtained from dulcite by all the processes used to obtain mannitane from mannite. Its formula is ($C^6H^{12}O^5$).

When left in free air, dulcitane, which is syrupy, is transformed into crystals of dulcite. When heated with acids, it combines with them, and gives the same neutral compounds as dulcite (dulcitanides).

To sum up, dulcite differs from mannite by its crystalline form, its point of fusion, which is situated at 182° instead of 165°, and its property of giving mucic acid when oxidized. The isomerism of mannite and dulcite is continued in the derivatives of these bodies.

HOOL OF
DICINE

### STUDY OF THE SUGARS.

**Glucose** ($C^6H^{12}O^6 + aq.$).—Glucose is widely distributed. It is found pure in the urine of diabetic persons, and mixed with levulose in honey and inverted sugar. It may be obtained from certain organic principles, such as salicin and arbutin, or by the action of dilute acids or diastase on starch. Cellulose may also be transformed into glucose under the influence of acids.

Gelatine, when treated by boiling dilute sulphuric acid, and chondrin, when submitted to the action of boiling concentrated hydrochloric acid, also give a sugar of the glucose series; but it is not yet known whether these sugars are identical with ordinary glucose.

Glucose may be prepared either from honey or from inverted sugar, or from diabetic urine, or, which is the method most used, from starch.

When honey or inverted sugar are left alone for a certain time, glucose is deposited in crystals. If the mass be then treated with cold alcohol, this removes the levulose which floats on the surface, and the glucose remains in an almost pure state.

In order to extract glucose from diabetic urine, the liquid is concentrated till crystals are deposited. These are washed with cold alcohol, then dissolved in water, and submitted to a new crystallization.

As is most frequently the case, when the object is, not to extract glucose in order to examine and analyze it, but to prepare this body, recourse must be had to the action which acids or diastase exercise on starch. If diastase be used, a mixture of water, starch, and germinated barley is heated to 70° until iodine no longer imparts a blue colour to the liquid, which is then filtered and evaporated to a syrupy consistence. Glucose crystallizes after a certain time.

When acids are used, a mixture is made of starch and dilute sulphuric acid, and heat is applied by means of a current of steam until iodine no longer colours the liquid blue, and alcohol does not precipitate it. The liquid is then saturated with carbonate of calcium, filtered and evaporated to the consistence of syrup, and left to crystallize.

Cellulose may be substituted for starch. This must first be dissolved in concentrated sulphuric acid, then the solution diluted with water, a part of the acid saturated, and finally the operation is completed by heating the mixture for about twelve hours to 100°.

The transformation of starch into glucose deserves attention. For a long time it was thought to be a simple hydration; it was believed that starch ($C^6H^{10}O^5$) was transformed into dextrin by a simple isomeric modification, and that dextrin then absorbed a molecule of water ($H^2O$) in order to be transformed into glucose. But it appears from a very important work recently published by M. Musculus, that in reality this is not the case. Diastase effects the division of starch into glucose and dextrin, and the operation may be compared to the saponification by water of ethers or fatty bodies. When the division of starch is completed, dextrin in its turn can be partially saccharified. This saccharification by diastase is always incomplete. With acids the phenomena are identical, with this slight difference, that the saccharification of the dextrin formed is much more easy.

Glucose is very soluble in water, though it is less so than cane sugar. One part of glucose requires one part and a third of cold water to dissolve it; it is also soluble in ordinary boiling alcohol, but less so in cold alcohol.

When an aqueous solution of glucose is evaporated, it assumes a syrupy state before crystallizing, and the crystals are only deposited after it has stood for some time.

Crystallized glucose is found in small lumps, and its crystals contain a molecule of water of crystallization, which they lose at 70° or 80° after having undergone aqueous fusion.

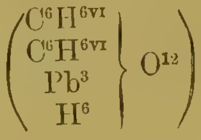
It is dextrogyrate, and its molecular rotatory power is equal to 56°.

Dry glucose is not altered by a temperature of 120° or even 130°. At 140° it loses water, and is transformed into caramel. If the heat be continued, it gives the same products of decomposition as cane sugar. Boiled for some time with dilute sulphuric or hydrochloric acid it is decomposed, and gives acids and ulmic compounds. When this decomposition takes place in contact with air, formic acid is also produced.

Cold concentrated sulphuric acid transforms glucose, without charring, into an allied acid.

Alkaline bases and earths readily combine with this sugar, but these compounds are very unstable and are destroyed at the boiling temperature. They are obtained by dissolving in a solution of glucose the base the glucosate of which is to be obtained, and it is then precipitated by alcohol. In this way have been obtained the glucosate of barium $[(C^6H^{12}O^6)^2(BaO)^3 + 2\ aq.]$ and the glucosate of calcium $[(C^6H^{12}O^6)^2(CaO)^3 + 2\ aq.]$.

Oxide of lead gives with glucose a compound which corresponds to the formula:



$$\left(\left.\begin{matrix} C^{16}H^{6\,\text{VI}} \\ C^{16}H^{6\,\text{VI}} \\ Pb^3 \\ H^6 \end{matrix}\right\} O^{12}\right)$$

A hot solution of glucose reduces cupro-potassic tartrate, and the mixture of potash and sulphate of copper when cold.

Glucose combines with chloride of sodium, and a crystallized compound is produced whose formula is $[(C^6H^{12}O^6)^2NaCl + aq.]$.

When glucose is boiled with binoxide of lead, formiate and carbonate of lead are produced, and carbonic anhydride is disengaged.

Chlorine and the perchlorides destroy glucose, charring it.

Butyric, acetic, stearic, and benzoic acids, when heated with glucose to 100° or 120° for fifty or sixty hours, combine with it, eliminating water, and give neutral bodies analogous to fats and to mannitanides: these are the glucosides of M. Berthelot.

**Levulose** ($C^6H^{12}O^6$).—Levulose is found mixed with glucose in inverted cane sugar, honey, and the sugar of acid fruits; it may be extracted from these mixtures by a very simple process which we owe to M. Dubrunfaut, and which consists in dissolving 10 grammes of inverted cane sugar in 100 grammes of water, and adding 6 grammes of slaked lime to the solution. At the end of some time the whole assumes the form of a thick liquid, which is squeezed in a press. The solid part is the calcareous salt of levulose. The whole of the glucose remains in solution. This calcareous salt dissolved in water and decomposed by a current of carbonic anhydride, furnishes pure levulose; the solution has only to be filtered and evaporated.

Levulose in a pure state is obtained with greater rapidity by saccharifying inulin by dilute acids: inulin is a principle isomeric with starch contained in the roots of elecampane, the dahlia, colchicum, and artichoke.

Levulose is syrupy, deliquescent, and uncrystallizable. It dissolves very readily in water and in ordinary alcohol, but with greater difficulty in absolute alcohol. It has a much sweeter taste than glucose.

It is levogyrate, and its rotatory power is $-106$ at 15°, but it varies greatly with the temperature; thus at 90° it diminishes by half, and becomes $-53$.

Glucose having, on the contrary, a rotatory power which does not vary with the temperature, the variations of the rotatory power of levulose ought to be found in inverted sugar, which is a mixture of equal weights of glucose and levulose. And, in fact, inverted sugar whose rotatory power is $-25$ at 15° becomes half as much at 52°, is null at 90°, and changes its sign above this temperature.

Levulose begins to decompose above 100°, and gives the same products of decomposition as glucose; with lime it forms an insoluble compound, the formula of which is $[(C^6H^{12}O^6)^2(CaO)^3.]$

Levulose decomposes more readily than glucose under the influence of acids or of heat; but it resists the action of ferments or alkalies much better. Its greater resistance to the action of ferments has been utilized in its preparation: if, during the course of a fermentation the rotatory power of the liquid be taken from time to time, it will be perceived that at the end of a certain time the deviation to the left attains its maximum and then diminishes: on arresting the fermentation at this moment, it will be found that all the glucose is destroyed, and that the liquid contains only levulose.

**Maltose** ($C^6H^{12}O^6$).—When glucose is obtained by diastase and starch, the product has a rotatory power in the same direction, but triple that of ordinary glucose. By the prolonged action of dilute acids, maltose is transformed into this latter sugar, and the differences between them do not appear to us sufficient to make a separate sugar of maltose. It is not an isomer, but merely an allotropic state of glucose.

**Galactose** ($C^6H^{12}O^6$).—When lactose is boiled for a long time with dilute mineral acids, it is transformed into a new sugar which ferments very readily, called galactose.

It presents the general reactions of the sugars with alkalies and cupro-potassic tartrate.

It crystallizes more readily than glucose; its rotatory power is to the right, equal to +83°·3; it is soluble in water and slightly soluble in cold alcohol. Its most remarkable distinctive characteristic is, that when oxidized by nitric acid it furnishes mucic acid.

**Mannitose** ($C^6H^{12}O^6$).—It has already been said that when mannite is oxidized by platinum black, a mixture of mannitic acid and of a sugar which ferments readily is obtained. In order to separate this from mannitic acid we require to saturate by lime, precipitate by alcohol, evaporate the filtered liquid and precipitate a second time by alcohol, after having brought the solution to a syrupy consistence; it is again filtered and evaporated to dryness.

Mannitose is syrupy and is not crystallizable.

It exercises no action on polarized light, and presents all the reactions of the other sugars.

## POLYGLUCOSIC ALCOHOLS.

Chemists have not as yet succeeded in obtaining polyglucosic alcohols synthetically from glucose, this latter body not possessing sufficient stability; but the vegetable kingdom furnishes us with a certain number of isomeric compounds which all have the formula ($C^{12}H^{22}O^{11}$), and which evidently represent diglucosic alcohol. These compounds are: cane sugar or saccharose (ordinary sugar); melitose, extracted from Australian manna; trehalose, which is obtained from a Turkish manna called trehala; mycose, extracted from ergot of rye; melezitose, the sweet exudation from larch manna; lactose, or sugar of milk; and parasaccharose, obtained by transforming cane sugar by a special ferment.

One property of these sugars leaves no doubt as to their constitution: they are capable of furnishing by hydration two molecules of one sugar or of two isomeric sugars. It is evident that if the division always gave rise to a single sugar it would be difficult to account for it. Fortunately, several of the compounds are divided into two isomeric sugars which may be separated, and the analogy of properties which exists among all these bodies permits the statement that the others undergo the same division, with the single difference that, instead of producing two distinct sugars, two molecules of one and the same sugar are formed.

It is by the hydration of saccharose and melitose that two different sugars are produced. With saccharose, glucose and levulose are formed; eucalyn and glucose are produced from melitose. The ferments which act readily on glucose and do not act on eucalyn, enable these two bodies to be separated. Levulose is separated from glucose by taking advantage of the slight solubility of the compound it forms with lime in comparison with the calcic compound of glucose, which is very soluble.

The rational formula which shows the splitting up of cane sugar and its isomers is:

$$\underset{\text{Cane sugar.}}{\left(\begin{array}{ll} C^{6}H^{6\text{vi}} & \left.\right\}(OH)^{5} \\ & \;O'' \\ C^{6}H^{6\text{vi}} & \left.\right\{(OH)^{5} \end{array}\right)} + \underset{\text{Water.}}{\left(\left.\begin{array}{l} H \\ H \end{array}\right\} O\right)} = \underset{\text{Glucose.}}{\left(\left.\begin{array}{c} C^{6}H^{6\text{vi}} \\ H^{6} \end{array}\right\} O^{6}\right)} + \underset{\text{Levulose.}}{\left(\left.\begin{array}{c} C^{6}H^{6\text{vi}} \\ H^{6} \end{array}\right\} O^{6}\right)}$$

It will be seen that these sugars are only diglucosic alcohols arising from condensation into a single molecule with elimination of water, either of two molecules of one sugar or of two molecules of two distinct sugars.

It will also be seen that cane sugar and its isomers are decatomic alcohols. However, the experimental demonstration of this fact presents great difficulties on account of the extreme instability of the compounds in question. It is nevertheless to be hoped that this problem may be solved, since M. Schützenberger has succeeded in preparing the acetic derivatives of cane sugar, starch, and cellulose, by heating these substances for some minutes with acetic anhydride at a temperature not exceeding the boiling point of this anhydride.

## STUDY OF THE PRINCIPAL POLYGLUCOSIC ALCOHOLS.

**Cane Sugar or Saccharose** ($C^{12}H^{22}O^{11}$).—Cane sugar exists in the juice of the sugar-cane, sorgho grass, maize, beetroot, carrot, and sugar maple. Until the last few years it was believed that acid fruits did not contain any trace of it; but, in 1861, M. Buignet showed, 1st, that the greater part of acid fruits contain a considerable portion of their saccharine matter in the state of cane sugar: 2nd, that that part which is not in the state of saccharose is in the state of inverted sugar, and as cane sugar alone furnishes inverted sugar, this demonstrates that the saccharine matter was always in the first instance saccharose; 3rd, that what produces the inversion in fruits is not the acid, but an organic substance which acts as a ferment; 4th, that, in all probability, the sugar is formed at the cost of the starch, and of a substance of the nature of tannin which exists in fruits.

Cane sugar is extracted from sugar-cane or beetroot. We will only describe the processes generally. In order to extract sugar from the cane, the juice is pressed out from the plant and heated with lime to separate the albuminous substances which are then separated in the form of froth (clarification); then it is evaporated and crystallized.

The sugar thus obtained is called *native* or *moist* sugar; it is then refined, the operation consisting in again dissolving the sugar in water, bleaching the solution by animal black in powder and bullock's blood, and crystallizing a second time after filtering.

The crystallization takes place in conical moulds. When it is finished the loaf is clarified by having syrup filtered through it. The saturated syrup cannot dissolve more sugar, but dissolves the foreign substances, and the loaf of sugar becomes perfectly white.

The processes used to extract sugar from beetroot are identical with the preceding, with this difference, that when the juice has been extracted and clarified, instead of evaporating it immediately, it is filtered through animal black in pieces.

In order to obtain sugar in large crystals (sugar-candy), its aqueous solution, previously evaporated to 37° of the areometer, is placed in a stove.

Cane sugar is soluble in every proportion in boiling water, and very soluble in cold water; its solutions form syrup before crystallizing; it is insoluble in absolute alcohol and ether; ordinary boiling alcohol dissolves it sparingly.

Cane sugar crystallizes in oblique rhomboidal prisms which are hemihedral, hard, and anhydrous. Its density is 1·606; it turns polarized light to the right, and its molecular rotatory power is $+73^\circ{\cdot}8$, and does not perceptibly vary with the temperature.

When cane sugar is heated, it melts at 106° without altering; but if the action of this temperature be prolonged, it divides into glucose and levulosane.

$$\begin{array}{ccccc} (C^{12}H^{22}O^{11}) & = & (C^{6}H^{12}O^{6}) & + & (C^{6}H^{10}O^{5}) \\ \text{Saccharose.} & & \text{Glucose.} & & \text{Levulosane.} \end{array}$$

This latter compound may be extracted from the mixture by destroying the glucose by fermentation and evaporating the solution. However, it is never obtained pure. Heated with dilute acids, this levulosane gives rise to levulose.

If saccharose be brought to a high temperature, products are formed which are called *caramelic acid*, *caramelan*, etc. These products are black; they cannot be purified, and appear to be the result of a molecular condensation.

Boiling dilute acids change the rotatory power of cane sugar, and transform it into a mixture of glucose and levulose which has received the name of *inverted sugar*.

If the action of boiling dilute acids on cane sugar be prolonged, and if these acids be energetic, humoid compounds are obtained.

Fatty organic acids, such as acetic, butyric or stearic acid, combine with sugar at 120°, forming neutral bodies analogous to the fatty bodies; tartaric acid also combines with saccharose under the same conditions. Concentrated sulphuric acid evolves heat with cane sugar, and the mass becomes black. On cooling a conjugate acid is obtained.

Boiling glacial acetic acid transforms saccharose in a few minutes into an acetic ether, which has not yet been analyzed.

Saccharose combines with potash, baryta, lime, etc. These compounds resist a temperature of 100°.

When lime is dissolved in sugar-water, a compound is produced the formula of which is ($C^{12}H^{22}O^{11}$,CaO), and which is very soluble. The solution of this body coagulates under the influence of heat, and a new compound is precipitated, which is tricalcic saccharose, the formula of which is [$C^{12}H^{22}O^{11}$,3(CaO)]; but if the liquid be allowed to cool, the precipitate is again dissolved.

Barytic saccharose ($C^{12}H^{22}O^{11}$,BaO), which is slightly soluble in water, has also been analyzed. On precipitating sugar-water by the ammoniacal acetate of lead, a body is obtained which has the formula ($C^{12}H^{18}Pb^{2}O^{11}$).

All these compounds, treated by carbonic anhydride in presence of water, re-form pure saccharose.

Solution of saccharose does not reduce cupro-potassic tartrate; nevertheless, this sugar possesses a certain reducing action in presence of alkalies: thus, on boiling oxide of silver with a mixture of sweetened water and an alkaline solution, metallic silver is obtained.

Chlorine attacks sugar at a temperature of 100°, and forms black compounds, which are but little known. Perchlorides act in the same manner. If cane sugar be left with bromine at the ordinary temperature the mass becomes syrupy, and the colour of the bromine disappears. At the end of a certain time this liquid becomes black, and is decomposed.*

Boiled with chloride of calcium or ammonium, sugar is inverted.

When cane sugar is submitted to the action of the yeast of beer, it ferments, but previously it becomes inverted. This fermentation is only complete when the solution is dilute.

If, instead of submitting sugar to the action of yeast, its aqueous solution, mixed with phosphate of ammonium, be left in contact with air, a ferment is developed differing from the yeast of beer which also transforms it into carbonic anhydride and alcohol; but the inversion takes place much more slowly—sometimes, even, it is not apparent. M. Jodin has remarked, that during the summer this particular fermentation is accompanied by an isomeric modification of saccharose, and produces a new sugar, which will be presently studied under the name of *parasaccharose.*

Cane sugar is a powerful agent for the preservation of animal and vegetable substances.

Under the influence of oxidizing agents it furnishes oxalic, saccharic, and tartaric acids.

INVERTED SUGAR.—It has been said that cane sugar becomes inverted under the influence of acids. The sugar which is thus formed is identical with that found in honey and in acid fruits. It is not crysllizable. When left alone for some time crystals of glucose are posited.

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* J. Vincent (unpublished).

We have seen, when speaking of levulose, how this latter body may extracted from inverted sugar, and have spoken of the modifications eat produces in its rotatory power.

In order to complete its study, and to demonstrate that this sugar is mixture of equal weights of glucose and levulose, it must be added, at when glucose is deposited in crystals from inverted sugar, the otatory power of the part that remains liquid becomes more strongly evogyrate, but that on the glucose being redissolved in this liquid by eans of gentle heat its original properties are restored.

**Melitose** ($C^{12}H^{22}O^{11} + 3$ aq.).—Melitose has been extracted by Berhelot from Australian manna, a sweet exudation produced by certain pecies of *Eucalyptus* of Van Diemen's Land.

It is readily prepared by treating this manna with water, bleaching he aqueous solution by animal charcoal, crystallizing, compressing the rystals between folds of bibulous paper, and purifying the product y a fresh crystallization.

The formula of crystallized melitose is ($C^{12}H^{22}O^{11} + 3$ aq.). At 100° t loses 2 aq., and at 130° it loses the third atom; but at this temperaure it begins to decompose; and if greater heat be applied, the residue is resolved into the usual principles which arise when sugars are decomposed by heat.

Melitose readily dissolves in water; its solutions do not become more syrupy before crystallizing, and are not precipitated by alcohol. They have a tendency to become covered with mould.

Melitose is dextrogyrate; its rotatory power is +102°; if it be heated for a quarter of an hour with sulphuric acid, this rotatory power is modified; but its direction is not changed, as is the case with saccharose.

Ammoniacal acetate of lead gives a precipitate in the solutions of melitose.

Melitose is not altered by the aqueous solution of baryta at 100°, and it exercises no reducing action on cupro-potassic tartrate, but boiling dilute sulphuric acid communicates this latter property to it.

Boiling fuming hydrochloric acid transforms this sugar into undetermined black substances.

If the liquid containing melitose modified by boiling dilute sulphuric acid be evaporated and saturated, a syrupy sugar is obtained which is not crystallizable, and which belongs to the glucose series.

Heated with nitric acid, melitose furnishes mucic and oxalic acids, which characteristic clearly distinguishes it from cane sugar. Under the influence of the yeast of beer it ferments, but does not give half the alcohol and carbonic acid which would be produced by an equivalent weight of cane sugar under the same conditions. When the fermentation is completed there remains in the liquid a saccharine principle incapable of fermentation, which is called eucalyn.

If, instead of submitting melitose to fermentation, the product furnished by this sugar when treated by dilute sulphuric acid be fermented, the same result will be obtained, except that only half the mass will be transformed into carbonic anhydride, alcohol, etc., and there will remain a weight of eucalyn equal to half the weight of the substance employed. This tends to prove that melitose thus modified forms a mixture of equal equivalents of eucalyn and a fermentable sugar. If this be the case, the rotatory power of this second sugar can be calculated by knowing those of eucalyn and of the modified melitose: such a calculation gives this new sugar a rotatory power about equal to that of ordinary glucose.

Thus, like cane sugar, melitose appears to have a complex grouping, and to contain the elements of two other more simple sugars.

**Trehalose** ($C^{12}H^{22}O^{11} + 2$ aq.). — Trehalose has been extracted by Berthelot from a Turkish manna, which is called *trehala*.

In order to prepare this saccharine principle, trehala is exhausted by boiling alcohol. Sometimes the trehalose crystallizes when the liquor cools; at others, the solution must be evaporated and left for several days in order to obtain crystals. These crystals should be compressed in blotting-paper and again dissolved in boiling alcohol, the solution bleached by animal black, and filtered. On cooling, the crystals are again deposited, and should be purified by one or two new crystallizations from boiling alcohol.

Trehalose crystallizes in hard rectangular octohedra, which have a sweet taste. Their formula is ($C^{12}H^{22}O^{11} + 2$ aq.). They lose their water of crystallization at 100°, and are then represented by the same formula as cane sugar.

If trehalose be briskly heated to 120° it melts; but if the heat be applied slowly, it is dehydrated without melting, and the temperature may be raised to 180° without decomposing this sugar, which is much more stable than saccharose or melitose.

Trehalose dissolves readily in water, and the solution becomes syrupy before crystallizing; it also dissolves in boiling alcohol, though in a less degree, very slightly in cold alcohol, and not at all in ether.

Trehalose is dextrogyrate: its molecular rotatory power is $+220°$; it is, therefore, triple that of cane sugar. It does not vary perceptibly with the temperature, and after twenty-four hours it remains the same as immediately after solution, even when this has been made with trehalose desiccated at 180°.

Boiling dilute sulphuric acid attacks trehalose with difficulty; on continuing the boiling for several hours, the rotatory power of the sugar is modified, becoming four times more active.

Trehalose does not ferment readily under the influence of yeast, but when it has been previously modified by dilute acid the fermentation becomes very easy.

At 100° trehalose is not altered either by potash or baryta, and it does not reduce the potassic tartrate of copper. Its aqueous solutions are precipitated by the ammoniacal acetate of lead. Fuming hydrochloric acid at 100° blackens trehalose; it is charred by concentrated sulphuric acid at the same temperature; nitric acid oxidizes it, producing oxalic acid but no mucic acid. At 180°, this sugar combines with stearic, benzoic, acetic, and butyric acids, and gives rise to bodies analogous to the glucosides, mannitanides, and the fatty bodies.

**Mycose** ($C^{12}H^{22}O^{11}$).—Mycose has been extracted from ergot of rye by Mitscherlich. He exhausted the powder with water, precipitated the solution by sub-acetate of lead, filtered, and removed the excess of lead by sulphuretted hydrogen. The solution when again filtered and evaporated to the consistence of a thick syrup deposits crystals of mycose, which are washed with cold alcohol and purified by several crystallizations.

Mycose resembles trehalose in its properties, with the exception of two:

It is not entirely dehydrated at 100°.

Its rotatory power is less than that of trehalose.

**Melezitose** ($C^{12}H^{22}O^{11}$).—Melezitose has been extracted by Berthelot from larch manna, a saccharine exudation of the larch (*Pinus laryx*).

In order to prepare this sugar, the manna is treated with boiling alcohol, and the solution evaporated to the consistence of an extract. At the end of several weeks, crystals are deposited which are pressed and purified by another crystallization from boiling alcohol.

These crystals seen through the microscope appear as oblique rhomboidal prisms. Their taste is less sweet than that of cane sugar; they possess a certain quantity of water of crystallization, but it has not been determined, as the crystals are very efflorescent. When desiccated at 110°, their formula is ($C^{12}H^{22}O^{11}$).

Melezitose melts at about 140°, and is destroyed at less than 200°, giving the same products of decomposition as the other sugars; it is very soluble in water, from which it is only deposited when its solution is of a syrupy consistence; it also dissolves sparingly in boiling lcohol, very little in cold alcohol, and not at all in ether.

Melezitose is dextrogyrate; its rotatory power is +94°·1. Under he influence of dilute acids, and especially of sulphuric acid, this otatory power is modified, and becomes similar to that of ordinary lucose. This modification requires about an hour for its production; ; therefore takes place more slowly than with cane sugar and quicker an with trehalose. It must be remarked that, whilst the action of ids splits up cane sugar and melitose into two different sugars, this me action appears only to produce a single sugar with trehalose and clezitose.

Alkalies do not alter melezitose at 100°, and the cupro-potassic tarte is not affected by it. Cold sulphuric acid chars it, and boiling drochloric acid soon turns it brown.

Melezitose is capable of undergoing alcoholic fermentation, but s takes place slowly and with difficulty. If however the action of the yeast be preceded by that of boiling dilute acids, the fermentation is readily produced.

Melezitose is oxidized by nitric acid, and oxalic acid is produced; but the production of mucic acid has never been observed in this reaction.

**Lactose** ($C^{12}H^{22}O^{11}+$ aq.).—Up to the present time lactose has only been obtained from the milk of the mammalia, from which it is extracted by coagulating the curd by a small quantity of sulphuric acid. The mixture is then filtered, evaporated, and crystallized. The crystals should be redissolved in water and their solution bleached by animal black, and then again submitted to crystallization.

Sugar of milk crystallizes in oblique rhomboidal prisms, of a density of 1·53. It is hard, transparent, gritty between the teeth, and has only a very slightly sweet taste; it dissolves in six parts of cold water, evolving heat, and in two and a half parts of boiling water.

Cold alcohol and ether do not dissolve lactose. The crystals when desiccated at 100° have the formula ($C^{12}H^{22}O^{11}+$ aq.). Heated to 150°, they lose their water of crystallization, and are then represented by the same formula as cane sugar. Moreover, at this temperature they commence to decompose, and at 170° are completely destroyed.

Sugar of milk produces right-handed rotation. This power, referred to the formula ($C^{12}H^{22}O^{11}$), is equal to $+59°·3$. It is stronger by 3·8 in recent solutions, but rapidly diminishes to attain the constant term.

When sugar of milk is heated with dilute mineral acids, or with strong organic acids, it is transformed into galactose and its rotatory power is modified.

Lactose is carbonized at 100° under the influence of fuming hydrochloric acid and of concentrated sulphuric acid. Gaseous hydrochloric acid combines with lactose, forming a grey mass, from which sulphuric acid displaces the sugar.

When oxidized by nitric acid, sugar of milk furnishes mucic and oxalic acids. Liebig has also proved the formation of saccharic and ordinary tartaric acids in this reaction.

Treated with a mixture of sulphuric and nitric acids, lactose gives a nitrous product which is insoluble in water and soluble in alcohol, from which it may be deposited in crystals. This product explodes at 100°.

Lactose combines with bases, such as soda or potash, in the proportion of one equivalent of sugar to three of base. These compounds are prepared by dissolving the alkali in the solution of milk sugar, and precipitating by alcohol.

Milk sugar may be extracted intact from these combinations when obtained cold; but if these latter be heated to 100° they become yellow, and are decomposed like the glucosates.

When sulphate of copper is dissolved in a solution of milk sugar, and a little potash added to the solution, a precipitate forms which again dissolves. If a greater quantity of potash be added, a deposit of sub-oxide of copper is produced: this reduction is assisted by gentle heat. Lactose also reduces cupro-potassic tartrate; but if quantities of glucose and lactose containing the same weight of carbon be taken, it is observed that milk sugar reduces less oxide of copper than glucose does. The quantities reduced are as 7 to 10.

Milk sugar does not ferment by the addition of yeast, but in presence of animal substances one portion of it is transformed into galactose, which undergoes alcoholic fermentation, while the greater part is transformed into butyric and acetic acids. According to Luboldt, a certain quantity of alcohol is always produced when milk sugar ferments between 15° and 20°; but in proportion as acidity is manifested the alcoholic fermentation becomes less intense, without however entirely ceasing.

The solution of milk sugar is precipitated by ammoniacal acetate of lead. Tartaric acid combines with lactose at the temperature of 100°.

**Parasaccharose** ($C^{12}H^{22}O^{11}$).—Parasaccharose is the sugar which is isomeric with cane sugar, the production of which, in a special fermentation of saccharose, we previously mentioned. The following are its properties:

Parasaccharose is very soluble in water without being hygrometric: alcohol at 90° does not perceptibly dissolve it.

At 100° it becomes coloured and appears to decompose slightly.

Desiccated in vacuo at 15° it corresponds to the formula ($C^{12}H^{22}O^{11}$). It is dextrogyrate: its rotatory power is about $+108°$ to 110°, and does not vary with the length of time the solution has been made.

Parasaccharose reduces cupro-potassic tartrate; but its reducing power is inferior to that of glucose, and even to that of lactose. Equal equivalents of these three sugars reduce quantities of oxide of copper which are as 10 : 7 : 5.

Like lactose, parasaccharose is therefore intermediate between the sugars which evidently belong to the family of saccharose and those which are grouped round glucose.

It is not modified by dilute sulphuric acid at 100°. Hydrochloric acid, on the contrary, imparts a brown colour to its solutions, raises its reducing power to the level of that of lactose, and lowers its rotatory power to that of saccharose.

## ANHYDRIDES OF POLYGLUCOSIC ALCOHOLS.

As to levulose there corresponds a known anhydride, levulosane, derived from it by the loss of ($H^2O$); and as anhydrides, little known, but derived in the same manner, correspond to the other sugars, so anhydrides derived by the elimination of one, two, three . . . *n* molecules of water should correspond to the di, tri . . . *n* glucosic alcohols.

Thus, if we establish the formulæ which the first anhydrides of the different polyglucosic alcohols should have, it will be seen that here,

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as with the anhydrides of glycols and condensed glycerines, these formulas are the multiples of each other:

$$\underset{\text{Glucose.}}{\left(C^6H^{6vi}\left\{(OH)^6\right.\right)} - \underset{\text{Water.}}{(H^2O)} = \underbrace{\left(C^6H^{6vi}\left\{\begin{matrix}O''\\(OH)^4\end{matrix}\right.\right) = (C^6H^{10}O^5)}_{\text{1st glucosic anhydride.}}$$

$$\underset{\text{Diglucosic alcohol.}}{\left(\begin{matrix}C^6H^{6vi}\\C^6H^{6vi}\end{matrix}\left\{\begin{matrix}(OH)^5\\O\\(OH)^5\end{matrix}\right.\right)} - \underset{\text{Water.}}{(H^2O)} = \underbrace{\left(\begin{matrix}C^6H^{6vi}\\C^6H^{6vi}\end{matrix}\left|\begin{matrix}O''\\(OH)^3\\O''\\(OH)^5\end{matrix}\right.\right) = (C^{12}H^{20}O^{10})}_{\text{1st diglucosic alcohol.}}$$

$$\underset{\text{Triglucosic alcohol.}}{\left(\begin{matrix}C^6H^{6vi}\\C^6H^{6vi}\\C^6H^{6vi}\end{matrix}\left\{\begin{matrix}(OH)^5\\O''\\(OH)^4\\O''\\(OH)^5\end{matrix}\right.\right)} - \underset{\text{Water.}}{(H^2O)} = \underbrace{\left(\begin{matrix}C^6H^{6vi}\\C^6H^{6vi}\\C^6H^{6vi}\end{matrix}\left\{\begin{matrix}O''\\(OH)^3\\O''\\(OH)^4\\O''\\(OH)^5\end{matrix}\right.\right) = (C^{18}H^{30}O^{15})}_{\text{1st triglucosic anhydride.}}$$

The formula ($C^6H^{10}O^5$) of the first glucosic anhydride is that adopted to represent the composition of a series of bodies which can all produce glucose by being hydrated.

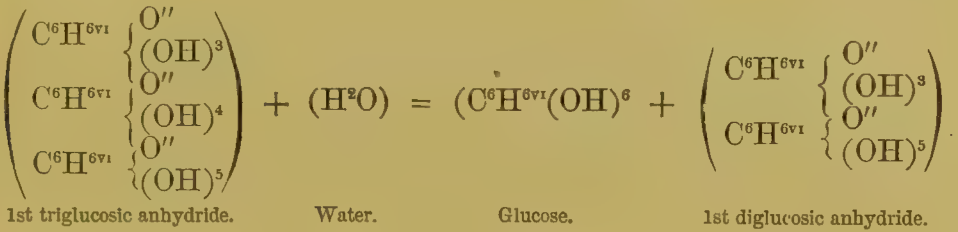
These bodies are different kinds of fecula and starch, which are designated by the general name of amylaceous substances; inuline, cellulose, dextrine, and gums.

Though having a constant composition, amylaceous matter, inuline and cellulose do not crystallize, and present a fibrous or cellular structure which is readily recognized under the microscope. They form a large portion of vegetable matter. Dextrine and the gums do not possess either an organized or a crystalline structure; they belong to that class of substances which are capable of forming masses, homogeneous throughout without being crystalline, and which are called *colloid bodies.*

The most simple formula that can express the constitution of these bodies is that of the first glucosic anhydride ($C^6H^{10}O^5$), but it is by no means certain that this formula really represents the weight of their molecule. Indeed, their organized, or at least their colloidal state appears to prove that their molecule corresponds to a formula the multiple of the preceding. These bodies would therefore be the first anhydrides of the polyglucosic alcohols. They might even be these alcohols themselves, because analysis cannot decide between two formulæ so nearly resembling each other as those of triglucosic alcohol ($C^{18}H^{32}O^{16}$) and that of its first anhydride ($C^{18}H^{30}O^{15}$).

In order to determine the degree of molecular complication of the different bodies in question, we must take into consideration the fact before mentioned, that in the saponification of the glucosic ethers the different substances which enter into their composition may be extracted one by one.

If, therefore, starch be a diglucosic anhydride, under hydrating influences it should at once be resolved into two molecules of glucose. But if starch be a triglucosic anhydride, or a triglucosic alcohol, it ought, under the influence of weak reagents, to divide first into glucose and diglucosic alcohol or anhydride, which by a further action would then be transformed into two molecules of glucose:



$$\underset{\text{1st triglucosic anhydride.}}{\left(\begin{matrix} C^6H^{6\text{vi}} \left\{\begin{matrix} O'' \\ (OH)^3 \end{matrix}\right. \\ C^6H^{6\text{vi}} \left\{\begin{matrix} O'' \\ (OH)^4 \end{matrix}\right. \\ C^6H^{6\text{vi}} \left\{\begin{matrix} O'' \\ (OH)^5 \end{matrix}\right. \end{matrix}\right)} + \underset{\text{Water.}}{(H^2O)} = \underset{\text{Glucose.}}{(C^6H^{6\text{vi}}(OH)^6} + \underset{\text{1st diglucosic anhydride.}}{\left(\begin{matrix} C^6H^{6\text{vi}} \left\{\begin{matrix} O'' \\ (OH)^3 \end{matrix}\right. \\ C^6H^{6\text{vi}} \left\{\begin{matrix} O'' \\ (OH)^5 \end{matrix}\right. \end{matrix}\right)}.$$

The latter is the case observed. M. Musculus has seen that when diastase acts on starch, this splits up into dextrine and glucose. Under the influence of dilute acids at a temperature of 100°, dextrine in its turn is transformed into glucose. Starch ought consequently to be considered as a triglucosic alcohol or anhydride. When hydrated it gives glucose and dextrine, which represents a diglucosic anhydride; then this is resolved into two new molecules of glucose; starch ought therefore to be represented by one of the two formulæ $(C^{18}H^{32}O^{16})$ or $(C^{18}H^{30}O^{15})$.

It is evident that if starch be a product of condensation, cellulose must also be one, since its structure is still more organized. It is not known whether several kinds of cellulose exist or not. At present only one is known. But alkalies and boiling acids are used to purify it, and these means may possibly reduce to this one state products much more complicated.

However this may be, a division similar to that undergone by starch has not been observed in the saccharification of the only cellulose known, and nothing can therefore be concluded as to the degree of condensation of this body.

These remarks on starch and cellulose, though still resting only on hypotheses, are of great importance. If the conclusions they present should be strictly proved, these bodies would no longer be regarded as giving rise to the sugars, but as being generated by them.

Moreover, if the immediate nitrogenized principles of animals and vegetables, such as the albuminous substances and gelatine, be ammoniacal derivatives of the sugars, as certain experiments give reason to suppose, the sugars are the centres of production of all organized substances—the principal elements of organized bodies.

These questions are doubtless very obscure, and do not at present admit of solution; but the hypotheses are deduced from known facts so logically, and are of such importance, that I thought it necessary to mention them here.

The compounds just reviewed as representing the classes of tetr-, pent-, and hex-atomic alcohols, have hitherto been included under the name of sugars. Thus erythrite, mannite, dulcite, the glucoses, cane sugar and its isomers were sugars. We have not thought it advisable to retain this general denomination, which is not based on any well-defined common characters.*

## STUDY OF THE PRINCIPAL POLYGLUCOSIC ANHYDRIDES.

**Cellulose** $(C^6H^{10}O^5)n$. — Cellulose forms the basis of vegetables, in which it is mixed with different incrusting matters and mineral salts; it also forms part of the substance known as chitin which constitutes the skin of the animals belonging to the class annulata.

The composition and chemical reactions of cellulose are always the same; but there are properties which depend on its state of aggregation, and which vary according to the vegetables whence it is extracted.

Cotton, paper, and old linen, which are almost entirely composed of it, are used in the preparation of cellulose, these bodies being freed from the incrusting matter they still contain. To effect this, they are boiled with a weak solution of potash, washed, and suspended in water, and a current of chlorine is transmitted through this liquid. They are then boiled a second time with weak potash, washed with acetic acid, then with boiling water, and finally with alcohol and ether, after having been previously dried at 100°; they are then considered as pure cellulose.

Pure cellulose is a white, diaphanous solid, insoluble in cold water, alcohol, ether, and the oils: its density is 1·525.

Cellulose dissolves in the blue liquid obtained by leaving pieces of copper in ammonia exposed to the air; hydrochloric acid precipitates it from this solution, but an excess of the reagent redissolves the precipitate.

When pure, air does not affect it; in wood, and under the simultaneous influence of the nitrogenized substances with which it is mixed, air and moisture, it undergoes slow combustion, and is transformed into a brown friable substance.

When brought into contact with sulphuric or concentrated phosphoric acid, cellulose dissolves without becoming coloured. If water be added to the liquid, the acid saturated with baryta, and any excess of baryta removed by a current of carbonic gas, the liquid, when filtered and evaporated, leaves a gummy residue, insoluble in water, which is isomeric with cellulose, and is known as dextrine.

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* See "*Des Sucres*," par A. Naquet.

Concentrated nitric acid acts on cellulose, producing nitrous derivatives. That resulting from the most advanced substitution answers to the formula $(C^{6n}H^{5n}(NO^2)^{5n}O^{5n})$. These products are very explosive. That prepared by means of cotton is called pyroxylin, or gun-cotton. It has been proposed to substitute it for gunpowder, but it is very liable to burst fire-arms.

Gun-cotton is soluble or insoluble in a mixture of alcohol and ether, according to whether the substitution of which it is the result is more or less complete. When soluble, it gives a thick product—collodion, which adheres to substances with which it is brought in contact. Collodion is used in surgery to unite the edges of wounds, and in photography to fix impressionable substances on the surface of glass.

According to Béchamp, nitric cellulose is reduced to the state of ordinary cellulose when submitted to the action of reducing agents. When distilled in a closed vessel with potash moistened with water, it gives hydrogen and wood-spirit; melted with potash it gives potassic oxalate.

Pure cellulose is not coloured blue by iodine; but when it has undergone a commencement of disaggregation by means of concentrated sulphuric acid, it becomes blue on the action of iodine.

Cellulose also dissolves in boiling glacial acetic acid, giving a compound ether which has not yet been analyzed.

**Amylaceous Matter** $(C^6H^{10}O^5)n$.—This substance is found deposited in grains in certain parts of plants, especially in the perisperm and cotyledons. The amylaceous matter extracted from potatoes is called fecula, and that obtained from the cereals is named starch. The fecula of certain tropical plants is also used as arrow-root, sago, tapioca, etc.

In order to extract the fecula contained in potatoes, these must be grated, and a stream of water directed on the pulp placed on a sieve; the fecula is carried away by the water into a receiver, at the bottom of which it is deposited. The water is decanted, and the deposit is washed two or three times with fresh water, and dried.

For laboratory purposes, in order to obtain fecula in a perfectly pure state, it is boiled in alcohol holding in solution 0·001 of caustic potash in order to remove a small quantity of fatty matter, and finally it is washed with alcohol and with water, and dried.

Wheat starch is now extracted in a similar manner; the flour is made into paste with water, and this paste placed on a sieve and submitted to the action of a jet of water. Formerly the paste was fermented, the nitrogenized matters became soluble, and the starch was obtained by washing the residue of the fermentation. This method gave less product than the present process, and was unhealthy on account of the fœtid emanations which exhaled during the fermentation.

Amylaceous matter constitutes a true organized material; seen under the microscope, it appears formed of small grains. These grains are composed of layers, which are closely superimposed, and are distinguished from each other by their densities: they are disposed symmetrically round a point of the superficies of the globule, which point is called the *hilum* or *umbilicus*.

The size and form of the amylaceous grains differ considerably according to the plant from which they are extracted. Their source may generally be determined by carefully examining their form under the microscope, and measuring their diameter.

Amylaceous matter is insoluble in cold water; hot water penetrates it, its globules swell, and it is converted into a gelatinous matter. When this is diluted by water and filtered it gives a liquid which colours iodine blue. It was therefore believed that disaggregated amylaceous matter was soluble in water; but Payen has shown that this is not the case. This phenomenon is entirely owing to the amylaceous substance passing through the filters. If hyacinth bulbs are plunged into such a liquid, the water alone penetrates them by endosmosis, and the starch is deposited upon them in a solid state.

Dilute acids entirely disaggregate the different species of fecula, and transform them into a soluble gummy substance known as dextrine, the same as is produced by the disaggregation of cellulose. The same transformation of amylaceous matter is also effected simply by the influence of a temperature of 160°.

Certain albuminous substances in decomposition, such as diastase which is found in germinated barley, produce the same metamorphosis when they are heated to 70° with water and starch; in this case the amylaceous matter appears clearly to be divided into glucose and dextrine.

Concentrated sulphuric acid rubbed up with amylaceous matter gives a compound acid containing the elements of the two bodies less one or more molecules of water; when hot this mixture becomes charred. Nitric acid of the density of 1·5 dissolves starch; water poured into this solution gives a white precipitate known as xyloidin, and which is only a nitric derivative answering to the formula $[C^6H^9(NO^2)O^5]^n$.

Starch, when mixed with water and albuminoid matters, undergoes lactic and butyric fermentations.

Like cane sugar and cellulose, starch dissolves in glacial acetic acid, and gives acetic ethers which have not yet been analyzed.

**Dextrine** $(C^6H^{10}O^5)^n$.—Dextrine is a product of the disaggregation of different kinds of starch or cellulose. It has already been seen how it may be procured from these substances.

It is a gummy body, soluble in water, which it renders viscid. Its solution strongly deviates the plane of polarized light to the right, from which property its name is derived. It is perfectly insoluble in alcohol, which indeed precipitates it from its aqueous solution.

When a little potassic hydrate and a few drops of a dilute solution of sulphate of copper are added to a solution of dextrine, the mixture becomes white; at 85° it deposits red crystalline sub-oxide of copper. This reaction clearly distinguishes dextrine from gum. Its aqueous solution is not precipitated either by the acetate or the sub-acetate of lead, but, if ammonia be added, a plumbic compound is precipitated whose formula is $(C^6H^{10}O^5,PbO)$.

Boiled for several hours in dilute hydrochloric or sulphuric acid, dextrine absorbs the elements of water, and is converted into glucose.

$$\underset{\text{Dextrine.}}{(C^6H^{10}O^5)} + \underset{\text{Water.}}{(H^2O)} = \underset{\text{Glucose.}}{(C^6H^{12}O^6)}$$

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## APPENDIX TO HEXATOMIC ALCOHOLS.

**Saccharometry.**—The object of saccharometry is: 1st, to determine whether a body contains cane sugar or a sugar of the glucose series; 2nd, to ascertain whether cane sugar be mixed with glucose; 3rd, to determine the proportions of these substances present, whether single or mixed.

Cane sugar or glucose may be readily detected by submitting the liquid containing them to the action of yeast. Alcohol and carbonic anhydride are formed.

Glucose is also easily recognized by means of reagents which will be spoken of presently, by the aid of which cane sugar can also be detected after having been inverted by boiling dilute sulphuric acid, or by hydrochloric acid.

In order to discover the presence of glucose, either alone or mixed with cane sugar, one of the following processes may be employed.

On boiling the saccharine solution with potash or soda, it becomes brown if glucose be present. It is best to use the double tartrate of potassium and copper in alkaline solution, as this reagent is not affected by being boiled with cane sugar, whilst glucose or inverted sugar in these conditions precipitate the red sub-oxide of copper. This test is very delicate.

The employment of bichromate of potassium has also been recommended. This is mixed with the saccharine solution while boiling. As the mixture cools it turns green if cane sugar be present. The solution of glucose does not under these circumstances assume a green shade, and if the cane sugar contain only a third of its weight of glucose the green colour which characterizes it will not be manifested. Below this proportion glucose does not prevent the coloration, but its intensity is not so great as it would be if the sugar were pure.

The most important part of saccharometry is the determination of the proportions of sugar and glucose. The methods used to effect this are founded on either the chemical or the physical properties of these bodies.

Chemical Processes.—1st. *Fermentation.*—This method of analysis is not exact, and is no longer used It consisted in fermenting a known weight of pure sugar, and measuring the carbonic anhydride formed, or of estimating the quantity of alcohol by means of the hydrometer. The substance to be analyzed was fermented, and the weight of sugar was deduced from the volume of carbonic anhydride or the quantity of alcohol it furnished.

When the substance contained both glucose and sugar, the weight of the two was first ascertained by fermentation, then the glucose was destroyed by boiling with an alkali for a few minutes, when a second fermentation gave the weight of the cane sugar, and the difference that of the glucose.

2nd. *Barreswil's Process.*—This process is now preferred; it is based on the reduction of alkaline solutions of the salts of copper by glucose. A solution is made of 40 gr. of pure crystallized sulphate of copper, 600 or 700 gr. of the solution of caustic soda of a density of 1·12, and 160 gr. of neutral tartrate of potassium dissolved in a little water. The cupric solution is gradually poured into the alkaline liquid, and the mixture is diluted by a volume of water sufficient to cause it to occupy 1154·4 cubic centimetres at a temperature of 15°.

In order to determine the strength of this liquid, a certain weight of sugar-candy is inverted; after measuring the volume of the solution, it is placed in a graduated glass, and poured drop by drop into a small flask containing 10 cubic centimetres of the cupric solution added to 40 of distilled water, and boiled. A yellow precipitate first forms, then a red one, which sinks to the bottom of the vessel. The process is discontinued when the cupric solution is decolorized, and from the quantity of saccharine solution employed the weight of the sugar which corresponds to 10 cubic centimetres of this cupric solution is deduced. Generally, when the solution has been prepared in the proportions indicated, 10 cubic centimetres correspond to 0·050 of dry glucose.

This proportion being once ascertained, nothing is easier than to determine the quantity of sugar contained in a liquid, provided that it do not also contain bodies capable of reducing the cupro-potassic tartrate. We have only to examine, by the operation just described, how much of this saccharine liquid is required to decolorize a given volume of the reagent.

If a mixture of cane sugar and a reducing sugar is to be analyzed, the proportion of the latter must first be determined, then the cane sugar is inverted, and a new determination is made. On subtracting from the total quantity of sugar obtained in this second operation that of the reducing sugar given by the first, the difference will give the cane sugar.

In order to complete the description, the processes of MM. Peligot and Dubrunfaut must be mentioned.

3rd. *Peligot's Method.*—M. Peligot advises the saturation of lime by the saccharine liquid, then the determination of the proportion of this base by a volumetric solution of sulphuric acid, and the deduction of the quantity of sugar from that of the lime. This process does not give exact results, because the saccharate of calcium dissolved in water has not a constant composition.

4th. *Dubrunfaut's Method.*—This process is much more exact. Dubrunfaut advises that the liquid to be analyzed be boiled with a volumetric solution of caustic soda. Then the soda which remains free is determined by means of a volumetric solution of sulphuric acid, which enables us to calculate the weight of the alkali which has entered into combination with the acids derived from the glucose. The weight of this latter sugar is thence deduced, the relation between the weight of glucose and that of soda transformed into the neutral salt having been determined by a previous experiment.

When this first operation is concluded, a second portion of the liquid to be analyzed is boiled with dilute sulphuric acid to invert the saccharose, and from the matter obtained the proportion of the reducing sugar is again determined by the same process. It is necessary in this case to deduct from the weight of the soda combined, that which has served to saturate the sulphuric acid, the solution of which was volumetric. The amount of the cane sugar is determined by the difference.

OPTICAL SACCHAROMETRY.—We have already (page 9) given a brief general explanation of the action of bodies on polarized light, and what is meant by their being levogyrate or dextrogyrate.

Biot has stated that, when a substance deviates the plane of polarization of light, there is always a direct relation between the deviation observed and the thickness of the substance, its density, and its specific rotatory power. This specific power is, in other words, the deviation of the plane of polarization which the substance in question would produce if its thickness were equal to unity, and if its density were also brought to unity by a suitable modification of the distance of its molecules.

It results from the above definition that the molecular rotatory power of a substance of known density $d$, and thickness $l$, will be obtained by dividing the deviation observed $a$ by the density and thickness, as the following equation indicates :

$$(1.) \qquad r = \frac{a}{dl},$$

in which $r$ is the specific rotatory power sought for.

In a solution let $d$ represent the density of the active substance dissolved. This density may be easily calculated, the weight of the substance $p$ and the volume of the solution $v$ being known ; the active substance occupies the same volume as the solution, and its density is given by the equation :

$$(2.) \qquad d = \frac{p}{v}.$$

If $d$ in the first equation be replaced by its equivalent it becomes :

$$(3.) \qquad r = \frac{a}{\frac{pl}{v}} = \frac{av}{lp},$$

which equation enables $r$ to be determined when $a$, $v$, $l$, $p$ are known. Conversely, if $r$ were known, and one of the equivalents $a$, $v$, $l$, $p$ were unknown, it might be determined in the same way; for instance, the weight would be given by the equation:

$$p = \frac{av}{rl}. \tag{4.}$$

Let us apply these remarks to the analysis of the sugars.

We know that cane sugar is dextrogyrate and that its specific rotatory power is $+ 73 \cdot 8$; if we have a solution of this body, and this solution when observed by the polarimeter in a tube the capacity and length of which are known, gives a deviation $= a'$, we should only have to replace in the fourth formula the general equivalents $a$, $v$, $r$, $l$ by those found in the experiment, and we should have the weight of sugar contained in the solution by the calculation.

Let us suppose that the cane sugar be mixed with glucose, which is dextrogyrate also; in order to find the respective quantities of these two sugars, it is necessary to determine the part belonging to each in the total rotation.

To arrive at this, the cane sugar is inverted by heating the solution for some minutes at 68° with $0 \cdot 1$ of hydrochloric acid; after which the deviation $b$, which the liquid gives, is again examined. But, as the state of dilution of this latter has been increased by the addition of the hydrochloric acid, the observed deviation $b$ must be replaced by $\frac{10}{9}$ of $b$.

We have then all the data necessary for the calculation.

The deviation $a'$ before the inversion was equal to the amount of the individual deviations $x$ of cane sugar and $y$ of glucose. After the inversion, $\frac{10}{9}\, b$ represents the deviation $y$ of glucose, which has not varied, diminished by the rotation to the left caused by the inverted sugar. This rotation is equal to $rx$, if it be admitted that a weight of cane sugar deviating by $x$ gives a quantity of uncrystallizable sugar deviating by $rx$ ($r$ having been determined by experiment).

The two following equations may be given for the determination of the two unknown terms:

$$\text{Before the inversion, } x + y = a'.$$

$$\text{After the inversion, } y - rx = b \times \frac{10}{9}.$$

If, instead of being mixed with glucose, cane sugar were mixed with inverted sugar which produces left-handed rotation, the above equations would assume the following form:

$$\text{Before the inversion, } x - g = a';$$

$$\text{After the inversion, } g + rx = b \times \frac{10}{9}:$$

*y* representing the deviation arising from the inverted sugar. As the rotatory power of this latter varies considerably with the temperature, Clerget has constructed tables of correction which enable the operation to be conducted at any temperature.

Biot's apparatus is often replaced by that of Soleil. This saccharometer, which need not be described, has a double quartz prism formed of two plates of quartz, one dextrogyrate and the other levogyrate, placed in front of the analyzing prism. These plates are both cut to an angle, and by causing one of them to rise or fall the thickness presented to the rays of light diminishes or increases. When they are on the same level these two plates exactly compensate each other, and if the analyzing prism be suitably placed, a perceptible tint (*teinte sensible*) is produced, which serves as a point of comparison.

When this apparatus is used it must be exactly regulated at the *teinte sensible*, and the tube containing the substance is placed in the passage of the ray of light. The tint is then destroyed, and in order to restore it the thickness of the plate of quartz of the same rotation as the substance examined must be diminished. A vernier scale indicates the precise decrease of thickness, whence the proportion of sugar contained in the solution is deduced. The quantity of sugar which, in a tube of known length and capacity, corresponds to a certain thickness of quartz is previously determined by experiment.

When the saccharometrical process just described can be applied it is the most exact of all. Unfortunately, the presence of active foreign substances, or the coloration of the liquids to be analyzed, often renders its use uncertain or impossible. However, in most cases, the action of colouring matters may be guarded against by precipitating with acetate of lead, and then filtering.

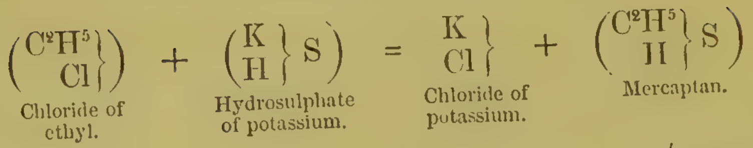
## MERCAPTANS AND THEIR ETHERS PROPER.

On substituting sulphur, selenium, or tellurium for oxygen in the alcohols of different atomicity, sulphuretted, seleniuretted, or telluretted alcohols are obtained, which are designated as mercaptans, seleniuretted mercaptans, and telluretted mercaptans.

Ethers proper correspond to these as to ordinary alcohols. These ethers are derived either by the substitution of an alcohol radicle for the typical hydrogen, as happens with monatomic mercaptans, or by the elimination of ($H^2S$), as is the case with biatomic mercaptans.

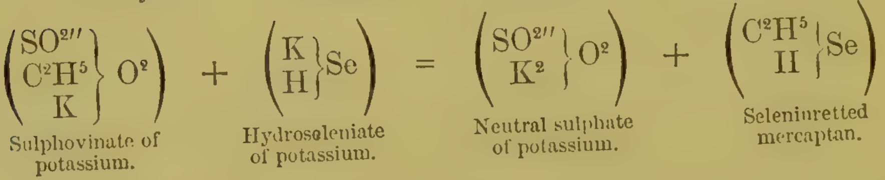
**Monatomic Mercaptans and their Ethers.**—Monatomic alcohols with the oxygen replaced by tellurium are not yet known, but those are known in which it is replaced by sulphur or selenium.

Mercaptans and seleniuretted mercaptans are prepared by distilling the acid salts of sulphuric ethers with hydrosulphate or hydroseleniate of potassium. The acid salt of sulphuric ether may be replaced by a hydrochloric or hydrobromic ether:



$$\left(\left.\begin{matrix}C^2H^5\\Cl\end{matrix}\right\}\right) + \left(\left.\begin{matrix}K\\H\end{matrix}\right\}S\right) = \left.\begin{matrix}K\\Cl\end{matrix}\right\} + \left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}S\right)$$

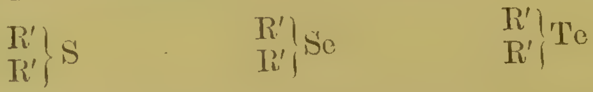
Chloride of ethyl. Hydrosulphate of potassium. Chloride of potassium. Mercaptan.



$$\left(\left.\begin{matrix}SO^{2''}\\C^2H^5\\K\end{matrix}\right\}O^2\right) + \left(\left.\begin{matrix}K\\H\end{matrix}\right\}Se\right) = \left(\left.\begin{matrix}SO^{2''}\\K^2\end{matrix}\right\}O^2\right) + \left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}Se\right)$$

Sulphovinate of potassium. Hydroseleniate of potassium. Neutral sulphate of potassium. Seleniuretted mercaptan.

On substituting a monosulphide, a monoselenide, or even a monotelluride for the alkaline hydrosulphate and hydroseleniate, the sulphides, selenides, and tellurides of alcoholic radicles are obtained, that is to say, the ethers proper of the mercaptans:

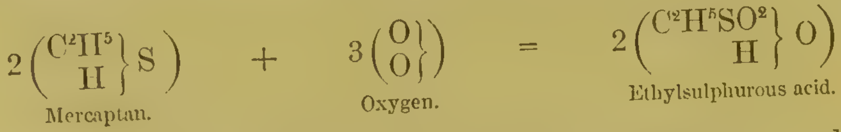


$$\left.\begin{matrix}R'\\R'\end{matrix}\right\}S \qquad \left.\begin{matrix}R'\\R'\end{matrix}\right\}Se \qquad \left.\begin{matrix}R'\\R'\end{matrix}\right\}Te$$

On replacing the monosulphides by bisulphides, bisulphides of the same radicles $\left.\begin{matrix}R'\\R'\end{matrix}\right\}S^2$ are formed.

Sulphuretted alcohols attack mercury, and their name originates from this (*mercurium captans*). They are fœtid bodies. Potassium and sodium may be substituted in them for hydrogen, the latter being set free. They undergo double decomposition with the greater part of metallic salts, giving precipitates which result from the replacement of their typical hydrogen by a metal.

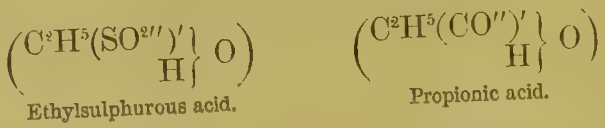
Mercaptans fix three atoms of oxygen under the influence of nitric acid:



$$2\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}S\right) + 3\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\right) = 2\left(\left.\begin{matrix}C^2H^5SO^2\\H\end{matrix}\right\}O\right)$$

Mercaptan. Oxygen. Ethylsulphurous acid.

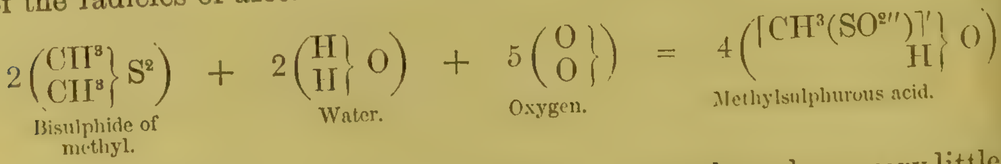
The bodies thus produced have been wrongly regarded as sulphurous acid ethers. They are rather monatomic acids, the radicle of which is formed by the addition of sulphuryl $(SO^{2''})$ to the alcohol radicle. They represent monobasic acids analogous to propionic acid, in which the biatomic group $(CO'')$ is replaced by the group $(SO^{2''})$:



$$\left(\left.\begin{matrix}C^2H^5(SO^{2''})'\\H\end{matrix}\right\}O\right) \qquad \left(\left.\begin{matrix}C^2H^5(CO'')'\\H\end{matrix}\right\}O\right)$$

Ethylsulphurous acid. Propionic acid.

These acids may also be prepared by the oxidation of the bisulphides of the radicles of alcohols:

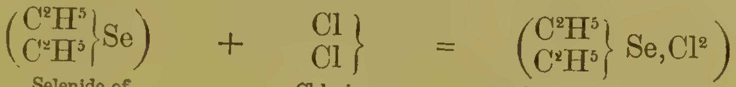


$$2\left(\left.\begin{matrix}CH^3\\CH^3\end{matrix}\right\}S^2\right) + 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + 5\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\right) = 4\left(\left.\begin{matrix}[CH^3(SO^{2''})]'\\H\end{matrix}\right\}O\right)$$

Bisulphide of methyl. Water. Oxygen. Methylsulphurous acid.

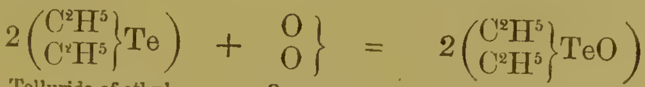
The seleniuretted mercaptans are fœtid. They have been very little studied. Their properties appear to be similar to those of their sulphuretted congeners.

The selenides and tellurides of alcohol radicles act the part of compound radicles. They can unite directly with chlorine, bromine, and oxygen:



$$\left(\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}Se\right) + \left.\begin{matrix}Cl\\Cl\end{matrix}\right\} = \left(\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}Se,Cl^2\right)$$

Selenide of ethyl. Chlorine. Chloride of selenethyl.



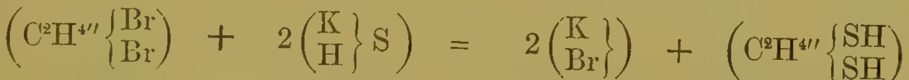
$$2\left(\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}Te\right) + \left.\begin{matrix}O\\O\end{matrix}\right\} = 2\left(\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}TeO\right)$$

Telluride of ethyl. Oxygen. Oxide of telluretbyl.

Their oxides undergo double decomposition with acids and give salts. The bibromides and bichlorides of selenethyl and telluretbyl demonstrate the tetratomicity of tellurium and selenium, of which atomicity their perchlorides ($SeCl^4$) and ($TeCl^4$) have already furnished proofs.

Quite recently M. Oefele has shown that the sulphide of ethyl may also act as a biatomic radicle. When it is heated with iodide of ethyl and a little water, it unites with this iodide and forms the compound ($[C^2H^5]^3SI$) which results from the direct union of the elements of its components. The iodine of this body may be replaced by chlorine, bromine, hydroxyl, etc., and a series of compounds all containing the monatomic radicle $(C^2H^5)^3S'$ are the result; the existence of such a radicle is another proof of the tetratomicity of sulphur which we were the first to assert.

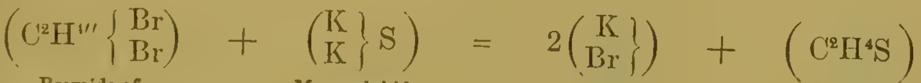
**Biatomic Mercaptans and their Ethers.**—Biatomic mercaptans, that is to say sulphuretted glycols, are obtained by causing the dibromhydrins of glycols to act on the alkaline hydrosulphates:



$$\left(C^2H^{4''}\left\{\begin{matrix}Br\\Br\end{matrix}\right.\right) + 2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}S\right) = 2\left(\left.\begin{matrix}K\\Br\end{matrix}\right\}\right) + \left(C^2H^{4''}\left\{\begin{matrix}SH\\SH\end{matrix}\right.\right)$$

Bromide of ethylene. Hydrosulphate of potassium. Bromide of potassium. Hydrosulphate of ethylene (ethylenic mercaptan).

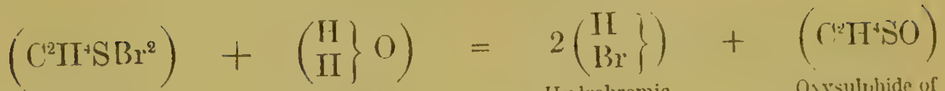
Their anhydrosulphides, that is to say the sulphides of their radicles, are prepared by substituting a monosulphide for the alkaline hydrosulphate in the preceding operation:



$$\left(C^2H^{4''}\left\{\begin{matrix}Br\\Br\end{matrix}\right.\right) + \left(\left.\begin{matrix}K\\K\end{matrix}\right\}S\right) = 2\left(\left.\begin{matrix}K\\Br\end{matrix}\right\}\right) + \left(C^2H^4S\right)$$

Bromide of ethylene. Monosulphide of potassium. Bromide of potassium. Sulphide of ethylene.

Only one of these bodies is well known, the sulphide of ethylene, which has been studied by M. Crafts. This chemist has found that this body combines directly with bromine, giving a bromide ($C^2H^4SBr^2$), which on contact with water is decomposed into hydrobromic acid and oxysulphide of ethylene.



$$\underset{\text{Bromosulphide of ethylene.}}{(C^2H^4SBr^2)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Hydrobromic acid.}}{2\left(\left.\begin{matrix}H\\Br\end{matrix}\right\}\right)} + \underset{\text{Oxysulphide of ethylene.}}{(C^2H^4SO)}$$

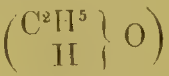
The same oxide ($C^2H^4SO$) is obtained by heating to 100° the sulphide of ethylene with monohydrated nitric acid. It is soluble in water and crystallizable. Potash decomposes it. At 150°, nitric acid transforms it into a new oxide, which is also crystallizable and which has the formula ($C^2H^4SO^2$). This latter is entirely insoluble in water; it dissolves in fuming nitric acid, from which it is precipitated by water; potash also dissolves it, and acids do not precipitate it from this solution. The alkalies appear therefore to transform it into a body possessing new and feebly acid properties.

**Triatomic Mercaptans (Sulphuretted Glycerines).**—These bodies have been obtained by the action of glyceric trichlorhydrins on the hydrosulphate of potassium. They are as yet imperfectly known.

## PSEUDO-ALCOHOLS.

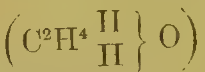
In the formulæ given for the alcohols, we have always admitted the existence of a radicle of an atomicity equal to the number of atoms of typical hydrogen contained in these alcohols. Liebig was the first to admit the presence of these radicles in the monatomic alcohols, which were then the only ones known. Dumas regarded the constitution of these bodies differently. He considered them as resulting from the union of water with a hydrocarbide analogous to ethylene.

Ordinary alcohol would be expressed according to these two theories by the following formulæ:



$$\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)$$

Liebig's theory.



$$\left(C^2H^4\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

Theory of Dumas.

Liebig's theory accounting for the reactions of the alcohols better than the other, the formulæ thence deduced were the only ones employed for some time; but recently M. Wurtz discovered a class of compounds, isomers of the true alcohols, the properties of which cannot be well understood except by attributing to them the formulæ Dumas formerly gave to the alcohols proper. Wurtz calls these bodies pseudo-alcohols.

Not only are pseudo-alcohols isomeric with the alcohols known, but pseudo-glycols, isomeric with the glycols, are also known; and probably for every degree of atomicity two parallel series exist.

*Preparation.*—1st. Whenever the second general method of preparing monatomic alcohols is applied to other hydrocarbides than ethylene and propylene, it gives rise, not to an alcohol but to a pseudo-alcohol: and this is the case whether the method by hydracids or that by sulphuric acid be employed.

2nd. It has been seen that on treating tetratomic hydrocarbides ($C^nH^{2n-2}$) with hydriodic acid they combine either with one or with two molecules of the acid. If these hydriodic derivatives be submitted to the action of acetate of silver, and the acetate formed be saponified by potash, a monatomic pseudo-alcohol having the formula ($C^nH^{2n-2},H^2O$) is obtained from the monohydriodic derivative, and a pseudo-glycol ($C^nH^{2n-2},2H^2O$) from the bihydriodic derivative.

Properties of Monatomic Pseudo-Alcohols.—1st. When a monatomic pseudo-alcohol is treated with concentrated sulphuric acid, it splits up into water and the hydrocarbide whence it arises. Under the same conditions, the alcohols proper produce a sulphovinic acid, which, when saturated with baryta, gives a crystallizable salt.

2nd. When heated to 200°-250°, the pseudo-alcohols split up into a hydrocarbide and water:

$$\underset{\text{Hydrate of amylene.}}{(C^5H^{10},H^2O)} = \underset{\text{Amylene.}}{(C^5H^{10})} + \underset{\text{Water.}}{(H^2O)}$$

The true alcohols present greater resistance to the action of heat.

3rd. Bromine added to a pseudo-alcohol displaces water and unites with the hydrocarbide. Chlorine gives the same reaction, but secondary products are also formed:

$$\underset{\text{Hydrate of butylene.}}{\left(C^4H^8,H^2O\right)} + \underset{\text{Bromine.}}{\left.\begin{matrix}Br\\Br\end{matrix}\right\}} = \underset{\text{Bromide of butylene.}}{\left(C^4H^8Br^2\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

Ordinary alcohols, on the contrary, lose $H^2$ in this case and give derivatives of substitution.

4th. Sodium disengages hydrogen for which it is substituted. In this case the pseudo-alcohols act in the same manner as the alcohols.

5th. When treated by hot acetic acid, in closed vessels, the pseudo-alcohols give water, amylene, and a very little of the acetic ether which corresponds to them.

6th. Cold hydrochloric, hydrobromic, and hydriodic acids decompose the pseudo-alcohols, giving rise to a hydrochlorate, hydrobromate, or hydriodate of their hydrocarbide, and water. These hydriodates are identical with those produced by the direct action of the hydracids on the hydrocarbides:

$$\underset{\text{Hydrate of amylene.}}{\left(C^5H^{10},H^2O\right)} + \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}} = \underset{\text{Hydrochlorate of amylene.}}{\left(C^5H^{10}\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

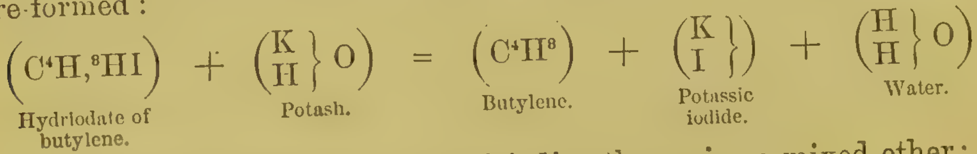
7th. Chlorhydrates, bromhydrates, or iodhydrates, have a lower boiling point than that of the simple ethers of the true alcohols, with which ethers they are isomeric.

8th. The iodhydrates react on moistened oxide of silver in the cold, while the hydriodic ethers of the true alcohols only react when hot. These latter only give in this reaction an alcohol and a little of its ether. The iodhydrates, on the contrary, give a product which is to the pseudo-alcohol what the ethers proper are to the alcohols, and a portion of the hydrocarbide is re-formed.

9th. The acetate of silver reacts only when hot on the hydriodic ethers of the alcohols, forming an acetic ether. When cold it reacts on the iodhydrates, giving an acetic ether of the pseudo-alcohol and re-forming a certain quantity of the hydrocarbide.

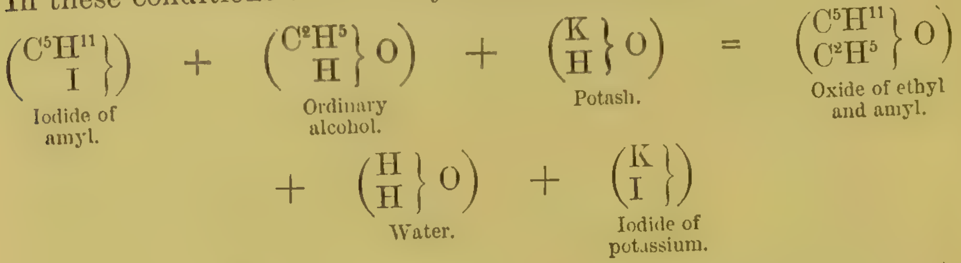
10th. The iodhydrates decompose by heat into hydriodic acid and hydrocarbide. The hydriodic ethers of the alcohols are much more stable.

11th The iodhydrates when heated with an alcoholic solution of potash give iodide of potassium, water and part of the hydrocarbide is re-formed:



$$\underset{\text{Hydriodate of butylene.}}{\left(C^4H,^8HI\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Butylene.}}{\left(C^4H^8\right)} + \underset{\text{Potassic iodide.}}{\left(\left.\begin{matrix}K\\I\end{matrix}\right\}\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

In these conditions the true hydriodic ethers give a mixed ether:



$$\underset{\text{Iodide of amyl.}}{\left(\left.\begin{matrix}C^5H^{11}\\I\end{matrix}\right\}\right)} + \underset{\text{Ordinary alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Oxide of ethyl and amyl.}}{\left(\left.\begin{matrix}C^5H^{11}\\C^2H^5\end{matrix}\right\}O\right)}$$

$$+ \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Iodide of potassium.}}{\left(\left.\begin{matrix}K\\I\end{matrix}\right\}\right)}$$

12th. The ethers proper derived from pseudo-alcohols, participate in the properties of these bodies. Heat splits them up, and hydriodic acid transforms them into water and iodhydrates. These characters distinguish them from the ethers of the true alcohols.

13th. Oxidants do not give ether acids or aldehyds with the pseudo-alcohols. Less carbonized substances are produced, which are mostly identical with those resulting from the direct oxidation of the hydrocarbide contained in the hydrate.

14th. The vapour density of the hydrochlorate of amylene corresponds to two volumes, as is the case with nearly all well-known bodies. At a high temperature this density corresponds to four volumes. In this case there has been decomposition, and free hydrochloric acid is found on opening the flask. Nevertheless, during the cooling, part of the acid and hydrocarbide again combine.

The properties of the monatomic pseudo-alcohols corresponding to the formula ($C^nH^{2n}O$) are imperfectly known. They appear to be analogous to the preceding.

PROPERTIES OF PSEUDO-GLYCOLS.—These properties have been less studied than those of the pseudo-alcohols. A single characteristic clearly distinguishes the pseudo-glycols from the glycols proper. Under the influence of hydrochloric acid, these latter only exchange (HO) for Cl and give chlorhydrins, whilst the pseudo-glycols exchange 2(HO) for $Cl^2$ and give the dichlorhydrins:

$$\underset{\text{Amyl-glycol.}}{\left(\left.\begin{matrix}C^5H^{10\prime\prime}\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Hydrochloric amyl-glycol.}}{\begin{matrix}\left(\left.\begin{matrix}C^5H^{10\prime\prime}\\H\end{matrix}\right\}O\right)\\Cl\end{matrix}}$$

$$\underset{\text{Bihydrate of diallyl.}}{\left(C^6H^{10}\left.\begin{matrix}H^2\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} = \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Bihydrochlorate of diallyl.}}{\left(C^6H^{10}\left.\begin{matrix}H^2\\Cl^2\end{matrix}\right\}\right)}$$

Constitution and Nomenclature.—Wurtz admits that in ordinary alcohols all the atoms of hydrogen except those that are typical are directly united to carbon, while the atoms of typical hydrogen are united to the atoms of oxygen which saturate the carbon by one of their affinities. It would be the same with pseudo-alcohols, except that in the radicle there would be atoms of hydrogen equal to the number of atoms of typical hydrogen, which would be more feebly united to the carbon than in the alcohols, and which consequently could be readily detached. Therefore, though the pseudo-alcohols cannot be considered as direct combinations of water with a hydrocarbide, these bodies act as if they were such combinations. In conformity with this hypothesis they may be represented by rational formulæ analogous to the following, which Wurtz proposes for the amylic pseudo-alcohol: $\left[(C^5H^{10})\left.\begin{matrix}H'\\H\end{matrix}\right\}O\right]$.

The diallylic pseudo-glycol, in order to be represented by a similar formula, ought to be written: $\left[(C^6H^{10})\left.\begin{matrix}H^{2\prime\prime}\\H^2\end{matrix}\right\}O_2\right]$

As, though they do not contain water already formed, these bodies act as if they did, they may be designated as hydrates of their fundamental hydrocarbides. Thus amylic pseudo-alcohol would be the hydrate of amylene, diallylic pseudo-glycol would be the dihydrate of diallyl, etc. The simple ethers of the pseudo-alcohols are called iodhydrates, bromhydrates, chlorhydrates, etc., of their hydrocarbides.

At present the following pseudo-alcohols have been prepared:

| | |
|---|---|
| Butylic pseudo-alcohol . . . . . . . . | $\left.\begin{matrix}[(C^4H^8)H]'\\H\end{matrix}\right\}O$ |
| Amylic pseudo-alcohol . . . . . . . . | $\left.\begin{matrix}[(C^5H^{10})H]'\\H\end{matrix}\right\}O$ |
| Hexylic pseudo-alcohol . . . . . . . | $\left.\begin{matrix}[(C^6H^{12})H]'\\H\end{matrix}\right\}O$ |
| Diallylic pseudo-alcohol . . . . . . . | $\left.\begin{matrix}[(C^6H^{10})H]'\\H\end{matrix}\right\}O$ |
| Diallylic pseudo-glycol . . . . . . . . | $\left.\begin{matrix}[(C^6H^{10})H^2]''\\H^2\end{matrix}\right\}O^2$ |

The octylic pseudo-alcohol has not been obtained. When treated by he oxide of silver, the iodhydrate of octylene gives octylene and very light traces of an oxygenated product.

There are bodies whose properties appear to resemble those of the pseudo-alcohols, such as peppermint, camphor or menthol ($C^{10}H^{20}O$), and the different hydrates of the essence of turpentine. Menthol would be a pseudo-alcohol of the ($C^{n}H^{2n}O$) series, and as this body cannot combine with nascent hydrogen, it should be considered as saturated.

## COMPOUND AMMONIAS.

The name of compound ammonias or amines is given to bodies which are derived from ammonia ($NH^3$) by the substitution of alcohol radicles for the hydrogen. There exist also organic bases which are derived in the same manner, not from ammonia ($NH^3$), but from the hydrate of ammonium $\left(\left.\begin{matrix}NH^4\\H\end{matrix}\right\}O.\right)$

Amines may be derived from one, two, three, four, *n* molecules of ammonia, and are called accordingly monamines or simply amines, diamines, triamines, tetramines, etc., to indicate their degree, of condensation.

Amines might therefore be classed according to this degree of condensation, and considered successively. But as polyatomic like monatomic alcohols may give rise to monamines, it will be more convenient to unite all the ammonias derived from alcohols of the same atomicity into one class, whatever may be their degree of condensation.

The nitrogen of organic bases may be replaced by phosphorus, arsenic, or antimony; from which substitution there arises a second class of bodies which may be considered intermediate between the nitrides of alcohol radicles and the combinations of these radicles with the metals and metalloids which do not belong to the nitrogenized group.

## AMINES DERIVED FROM MONATOMIC ALCOHOLS.

The radicles which may be derived from a monatomic alcohol are always monatomic. The amines of this class never therefore contain radicles the capacity for saturation of which is greater than *one*. They are always derived from a single molecule of ammonia, and are monamines.

In ammonia $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$, the hydrogen may be replaced either wholly or in part by the radicle of one alcohol or by radicles of different alcohols. From three different alcohol radicles R R′ R″, we may obtain the compounds:

$$\left.\begin{matrix}R\\H\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}R\\R'\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}R\\R'\\R''\end{matrix}\right\}N$$

Besides, in the hydrate of ammonium $\left(\left.\begin{matrix}NH^4\\H\end{matrix}\right\}O\right)$, the four atoms of hydrogen may be replaced by four alcohol radicles either different or identical; bases result whose widest formula is $\left(\left.\begin{matrix}RR'R''R'''N\\H\end{matrix}\right\}O\right)$.

Those bodies answering to the formula $\left.\begin{matrix}R\\H\\H\end{matrix}\right\}N$ are called primary monamines or amides; those of the form $\left.\begin{matrix}R\\R'\\H\end{matrix}\right\}N$ are called secondary monamines or imides bases; those of the form $\left.\begin{matrix}R\\R'\\R''\end{matrix}\right\}N$ are tertiary monamines or nitrile bases; and bodies of the fourth group, whose general formula is $\left.\begin{matrix}RR'R''R'''N\\H\end{matrix}\right\}O$, are generally designated as hydrates of quaternary ammoniums.

Preparation of the Primary Monamines.—These bodies may be procured by several processes, those of Wurtz, Hofmann, Zinin, and Mendius. Some of these compounds may be formed by special reactions which are not applicable to all the series.

*Wurtz's Process.*—When cyanic acid is distilled with an excess of alkali (*see* Cyanogen Compounds), an alkaline carbonate and ammonia are obtained:

$$\underset{\text{Cyanic acid.}}{\left(\left.\begin{matrix}CN\\H\end{matrix}\right\}O\right)} + 2\underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Carbonate of potassium.}}{\left(\left.\begin{matrix}CO''\\K^2\end{matrix}\right\}O^2\right)} + \underset{\text{Ammonia.}}{\left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right)}$$

If instead of causing potash to act with cyanic acid, that is to say, with the cyanate of hydrogen, a cyanic ether, in other words, the cyanate of an alcohol radicle be submitted to the action of this alkali, one of the three atoms of hydrogen which in the preceding reaction gave rise to the formation of ammonia is replaced by an alcohol radicle. The ammonia obtained therefore contains a radicle of alcohol substituted for hydrogen.

$$\underset{\text{Cyanic ether of a monatomic alcohol.}}{\left(\left.\begin{matrix}CN\\R\end{matrix}\right\}O\right)} + 2\underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic carbonate.}}{\left(\left.\begin{matrix}CO''\\K^2\end{matrix}\right\}O^2\right)} + \underset{\text{Primary monamide.}}{\left(\left.\begin{matrix}R\\H\\H\end{matrix}\right\}N\right)}$$

All the primary compound ammonias are obtained by distilling cyanic ethers with an excess of potash. The product is generally collected in hydrochloric acid, and when the hydrochlorate is obtained dry, the alkaloid is extracted by the same process as is used to obtain ammonia from sal-ammoniac.

*Hofmann's Process.*—Hofmann mixes an alcoholic solution of ammonia with the simple ether of an alcohol; there is then produced a primary compound ammonia, and a hydracid which remains united to this ammonia:

$$\underset{\text{Hydriodic ether.}}{\left(\left.\begin{matrix}R\\I\end{matrix}\right\}\right)} + \underset{\text{Ammonia.}}{\left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right)} = \underbrace{\left(\left.\begin{matrix}R\\H\\H\end{matrix}\right\}N,HI\right) = \left(\left.\begin{matrix}R\\H\\H\\H\end{matrix}\right\}N,I\right)}_{\text{Iodide of a primary compound ammonium.}}$$

The compound ammonia is then separated from the iodide formed by distilling this salt with lime.

Nitric ether may be substituted for simple ethers in this process.

*Process of M. Mendius.*—Mendius obtains primary ammonias by submitting hydrocyanic ethers to the action of nascent hydrogen. A base is thus produced which, on the replacement of hydrogen, contains, not the radicle which existed in the hydrocyanic ether, but its first higher homologue:

$$\underset{\text{Cyanide of methyl.}}{\left(\left.\begin{matrix}CH^3\\CN\end{matrix}\right\}\right)} + \underset{\text{Hydrogen.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}\right)} = \underset{\text{Ethylamine.}}{\left(\left.\begin{matrix}C^2H^5\\H\\H\end{matrix}\right\}N\right)}$$

*Zinin's Process.*—The preceding processes are applicable to all the series of which the alcohols are known. That of Zinin, on the contrary, can only be applied to the aromatic series and to the series less hydrogenized than it. It consists in treating the fundamental hydrocarbide of the series with nitric acid. A nitrogenized product will be obtained which, when submitted to the influence of reducing agents, loses its oxygen and fixes $H^2$. Thus an ammonia is produced containing the monatomic radicle derived from the hydrocarbide employed by the elimination of hydrogen:

$$\text{Ex.}\quad \underset{\text{Toluene.}}{(C^7H^8)} + \underset{\text{Nitric acid.}}{(NHO^3)} = \underset{\text{Nitro-toluene.}}{(C^7H^7(NO^2))} + \underset{\text{Water.}}{H^2O}$$

$$\underset{\text{Nitro-toluene.}}{C^7H^7(NO^2)} + \underset{\text{Hydrogen.}}{3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}\right)} = \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Toluidine.}}{\left(\left.\begin{matrix}C^7H^7\\H\\H\end{matrix}\right\}N\right)}$$

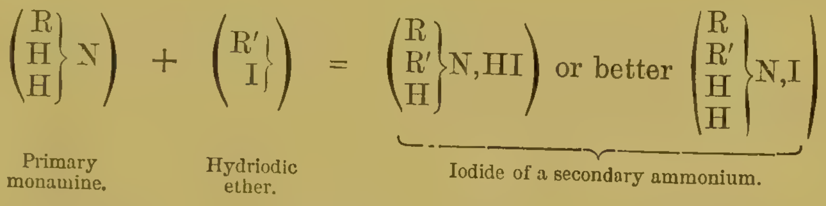
Different reducing agents may be employed. Sometimes the hydrosulphate of ammonia in alcoholic solution is used: in this case the ammonia is set free, the sulphur is deposited, and the nascent hydrogen produces the reaction indicated; sometimes the nascent hydrogen is disengaged by iron and acetic acid, sometimes by sodium amalgam, and sometimes from hydriodic acid, the iodine of which becomes free.

Recently, Cannizzaro has prepared the primary ammonia of the benzoic series by the processes of Messrs. Wurtz, Hofmann, and

Zinin. He found that the alkaloid obtained by the two first methods constitutes a single product, isomeric with that obtained by the third method. This latter differs from the other two, possessing a less marked basic character, and containing a phenic instead of an alcohol radicle. (*See* Phenols.)

Reactions which give rise to Primary Monamines. — When nitrogenized organic substances are submitted to distillation, either alone or in presence of a powerful alkali, the volatile alkaloids of this class are formed. Thus the oil of pit-coal contains aniline, and certain oxygenated vegetable alkaloids give methylamine when distilled with potash, etc. These reactions may be useful in the preparation of certain organic bases, but do not possess any general interest.

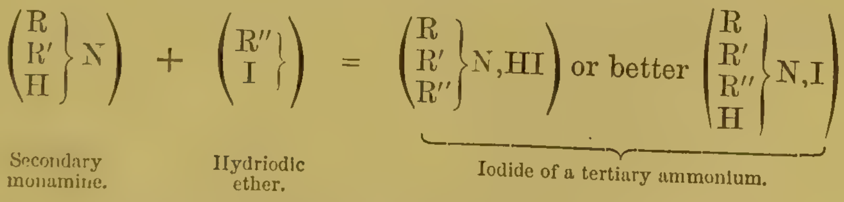
Preparation of Secondary Monamines.—Secondary monamines have as yet only been obtained by Hofmann's process. They are prepared by heating a mixture of a simple ether and a primary monamine in a hermetically-sealed tube. The reaction is the same as that which furnishes the primary ammonias by means of ammonia and a simple ether :



$$\underset{\text{Primary monamine.}}{\left(\left.\begin{matrix}R\\H\\H\end{matrix}\right\}N\right)} + \underset{\text{Hydriodic ether.}}{\left(\left.\begin{matrix}R'\\I\end{matrix}\right\}\right)} = \underbrace{\left(\left.\begin{matrix}R\\R'\\H\end{matrix}\right\}N,HI\right) \text{ or better } \left(\left.\begin{matrix}R\\R'\\H\\H\end{matrix}\right\}N,I\right)}_{\text{Iodide of a secondary ammonium.}}$$

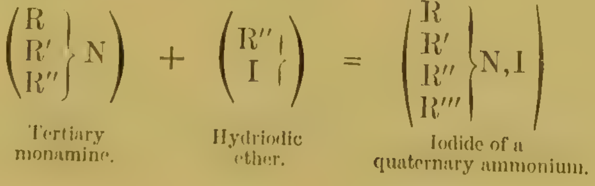
The base is then extracted from its iodide, as with alkaloids of the first degree.

Preparation of Tertiary Monamines.—These are also obtained by Hofmann's process. The secondary base is heated with a simple ether and the tertiary ammonia is taken from the iodide formed :



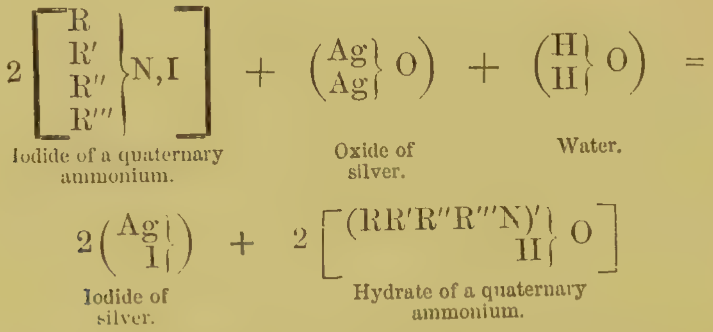
$$\underset{\text{Secondary monamine.}}{\left(\left.\begin{matrix}R\\R'\\H\end{matrix}\right\}N\right)} + \underset{\text{Hydriodic ether.}}{\left(\left.\begin{matrix}R''\\I\end{matrix}\right\}\right)} = \underbrace{\left(\left.\begin{matrix}R\\R'\\R''\end{matrix}\right\}N,HI\right) \text{ or better } \left(\left.\begin{matrix}R\\R'\\R''\\H\end{matrix}\right\}N,I\right)}_{\text{Iodide of a tertiary ammonium.}}$$

Preparation of Hydrates of Quaternary Ammoniums.—When a simple ether, especially hydriodic ether, is heated with a tertiary base, a direct combination takes place, and an iodide of a quaternary ammonium, which is generally crystallized, is obtained :



$$\underset{\text{Tertiary monamine.}}{\left(\left.\begin{matrix}R\\R'\\R''\end{matrix}\right\}N\right)} + \underset{\text{Hydriodic ether.}}{\left(\left.\begin{matrix}R''\\I\end{matrix}\right\}\right)} = \underset{\text{Iodide of a quaternary ammonium.}}{\left(\left.\begin{matrix}R\\R'\\R''\\R'''\end{matrix}\right\}N,I\right)}$$

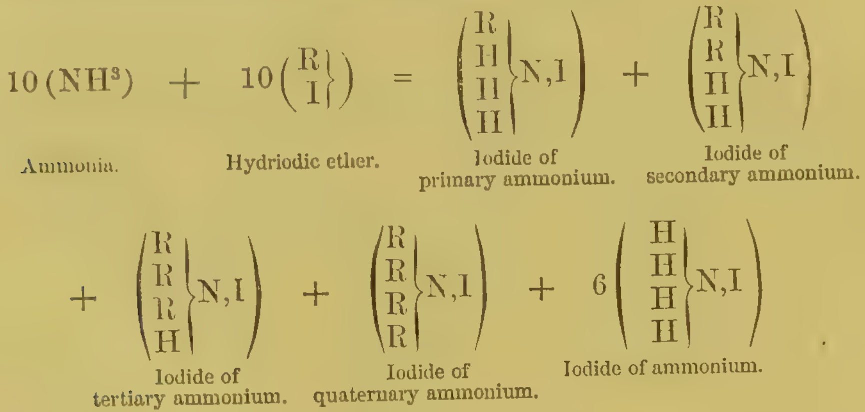
The hydrate of ammonium cannot be isolated by distilling the iodide with potash, as this hydrate is decomposed by distillation; but if oxide of silver be made to act on an aqueous solution of the iodide, iodide of silver is formed, and the hydrate sought for remains dissolved. On filtering the liquid and evaporating in vacuo it is obtained crystallized:



$$\underset{\text{Iodide of a quaternary ammonium.}}{2\left[\left.\begin{matrix}R\\R'\\R''\\R'''\end{matrix}\right\}N,I\right]} + \underset{\text{Oxide of silver.}}{\left(\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} =$$

$$\underset{\text{Iodide of silver.}}{2\left(\left.\begin{matrix}Ag\\I\end{matrix}\right\}\right)} + \underset{\text{Hydrate of a quaternary ammonium.}}{2\left[\left.\begin{matrix}(RR'R''R'''N)'\\H\end{matrix}\right\}O\right]}$$

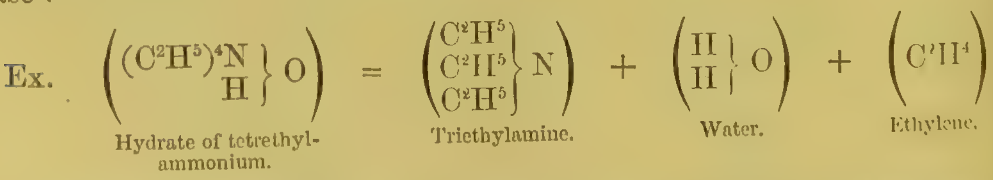
Separation of Monamines of different Degrees.—When an alcoholic solution of ammonia is submitted to the action of a simple ether, the reaction is far from being so simple as we have hitherto supposed. In reality, instead of only giving rise to a primary monanime, this reaction gives rise to all the degrees of substitution possible, and a mixture of the iodides of the primary, secondary, tertiary, and quaternary ammoniums is obtained, as the following equation indicates:



$$\underset{\text{Ammonia.}}{10(NH^3)} + \underset{\text{Hydriodic ether.}}{10\left(\left.\begin{matrix}R\\I\end{matrix}\right\}\right)} = \underset{\text{Iodide of primary ammonium.}}{\left(\left.\begin{matrix}R\\H\\H\\H\end{matrix}\right\}N,I\right)} + \underset{\text{Iodide of secondary ammonium.}}{\left(\left.\begin{matrix}R\\R\\H\\H\end{matrix}\right\}N,I\right)}$$

$$+ \underset{\text{Iodide of tertiary ammonium.}}{\left(\left.\begin{matrix}R\\R\\R\\H\end{matrix}\right\}N,I\right)} + \underset{\text{Iodide of quaternary ammonium.}}{\left(\left.\begin{matrix}R\\R\\R\\R\end{matrix}\right\}N,I\right)} + \underset{\text{Iodide of ammonium.}}{6\left(\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}N,I\right)}$$

In order to separate these different bodies, Hofmann first distils the whole with potash. The iodides are decomposed, free ammonia passes over, and the hydrate of quaternary ammonium which is formed is decomposed by the distillation, giving a new quantity of the tertiary base:



$$\text{Ex.}\quad \underset{\text{Hydrate of tetrethyl-ammonium.}}{\left(\left.\begin{matrix}(C^2H^5)^4N\\H\end{matrix}\right\}O\right)} = \underset{\text{Triethylamine.}}{\left(\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right\}N\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Ethylene.}}{\left(C^2H^4\right)}$$

The distilled product contains the ammonias of the three first degrees. This mixture is treated with the oxalate of ethyl. The primary base gives rise to a double decomposition, and a precipitate forms which is oxamide $\left(\left.\begin{matrix}C^2O^{2\prime\prime}\\H^2\\H^2\end{matrix}\right\}N^2\right)$, in which $H^2$ is replaced by two molecules of the radicle the base contained:

$$\underset{\text{Primary ammonia.}}{2\left(NH^2R\right)} + \underset{\text{Oxalate of ethyl.}}{\left(\left.\begin{matrix}C^2O^{2\prime\prime}\\(C^2H^5)^2\end{matrix}\right\}O^2\right)} = \underset{\substack{\text{Oxamide in which}\\ \text{R}^2\text{ take the place of H}^2.}}{\left(\left.\begin{matrix}C^2O^{2\prime\prime}\\R^2\\H^2\end{matrix}\right\}N^2\right)} + \underset{\text{Alcohol.}}{2\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)}$$

This precipitate when collected, washed with alcohol and with water, and distilled with potash, gives the primary base in a pure state:

$$\underset{\substack{\text{Oxamide in which}\\ \text{R}^2\text{ takes the place of H}^2.}}{\left(\left.\begin{matrix}C^2O^{2\prime\prime}\\R^2\\H^2\end{matrix}\right\}N^2\right)} + \underset{\text{Potash.}}{2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Oxalate of potassium.}}{\left(\left.\begin{matrix}C^2O^{2\prime\prime}\\K^2\end{matrix}\right\}O^2\right)} + \underset{\text{Primary base.}}{2\left(\left.\begin{matrix}R\\H\\H\end{matrix}\right\}N\right)}$$

The secondary ammonia also undergoes a double decomposition in presence of the oxalate of ethyl; oxamate of ethyl $\left(\left.\begin{matrix}\left[\left.\begin{matrix}C^2O^{2\prime\prime}\\C^2H^5\end{matrix}\right\}O\right]'\\H\\H\end{matrix}\right\}N\right)$ is produced, in which $H^2$ is replaced by two atoms of the radicle of the secondary ammonia:

$$\underset{\text{Oxalate of ethyl.}}{\left(\left.\begin{matrix}C^2O^{2\prime\prime}\\ [C^2H^5]^2\end{matrix}\right\}O^2\right)} + \underset{\substack{\text{Secondary}\\ \text{ammonia.}}}{\left(\left.\begin{matrix}R\\R\\H\end{matrix}\right\}N\right)} = \underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)} + \underset{\substack{\text{Oxamate of ethyl in which}\\ \text{R}^2\text{ is substituted for H}^2.}}{\left(\left.\begin{matrix}\left[\left.\begin{matrix}C^2O^{2\prime\prime}\\C^2H^5\end{matrix}\right\}O\right]'\\R\\R\end{matrix}\right\}N\right)}$$

This new liquid body is easily separated from the precipitate from which the primary ammonia is extracted; it is also readily separated from the tertiary ammonia, on which oxalate of ethyl does not act, these two bodies having very different boiling points.

This oxamate distilled with potash gives potassic oxalate, alcohol, and the secondary base. To separate this latter from the alcohol, it is saturated with hydrochloric acid, evaporated to dryness, and the base extracted from its hydrochlorate by means of lime:

$$\underset{\substack{\text{Oxamate of ethyl in which}\\ \text{R}^2\text{ is substituted for H}^2.}}{\left(\left.\begin{matrix}\left[\left.\begin{matrix}C^2O^{2\prime\prime}\\(C^2H^5)\end{matrix}\right\}O\right]'\\R\\R\end{matrix}\right\}N\right)} + \underset{\text{Potash.}}{2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Oxalate of potassium.}}{\left(\left.\begin{matrix}C^2O^{2\prime\prime}\\K^2\end{matrix}\right\}O^2\right)}$$

$$+ \underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)} + \underset{\substack{\text{Secondary}\\ \text{ammonia.}}}{\left(\left.\begin{matrix}R\\R\\H\end{matrix}\right\}N\right)}$$

LEEDS SCHOOL OF MEDICINE

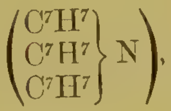
It has been seen that the tertiary base is readily extracted by fractional distillation, from the liquid mixture from which the primary base is precipitated. Submitted to the action of an hydriodic ether it furnishes the iodide of quaternary ammonium in a pure state.

PROPERTIES OF PRIMARY, SECONDARY, AND TERTIARY MONAMINES.—1st. In the free state all these compounds correspond to the ammonia type. Like ammonia itself, they unite directly with acids without elimination of water. The salts which form belong to the type of hydrate of ammonium, either simple or condensed, according to the atomicity of the acid which reacts.

2nd. When these bases are soluble, the primary are more so than the secondary, which in their turn are more so than the tertiary bases.

3rd. The primary bases are more strongly alkaline than the secondary, and these than the tertiary. We have an example of this in the benzilic bases recently prepared by Cannizzaro. Benzylamine

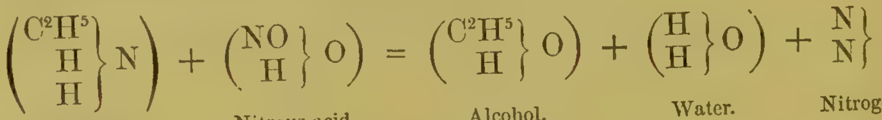
$\left(\left.\begin{matrix}C^7H^7\\H\\H\end{matrix}\right\}N\right)$ is such a powerful base that it absorbs directly the carbonic anhydride of the air. The tribenzylamine



$\left(\left.\begin{matrix}C^7H^7\\C^7H^7\\C^7H^7\end{matrix}\right\}N\right)$, on the contrary, has only a weak affinity for acids.

4th. When nitrous acid acts on a primary ammonia in aqueous solution, the radicle contained in the ammonia is transformed into its alcohol; water and free nitrogen are also produced.

Ex.

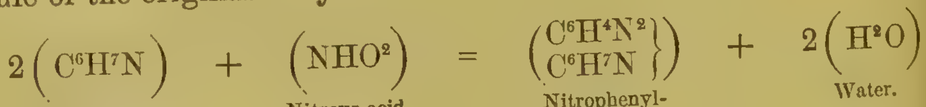


$$\left(\left.\begin{matrix}C^2H^5\\H\\H\end{matrix}\right\}N\right) + \left(\left.\begin{matrix}NO\\H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + \left.\begin{matrix}N\\N\end{matrix}\right\}$$

Ethylamine. Nitrous acid. Alcohol. Water. Nitrogen.

When nitrous acid acts on the alcoholic solution of an aromatic alkaloid of the radicle of phenol, nitrogen is substituted for three atoms of hydrogen, and the nitrogenized product remains combined with a molecule of the original body.

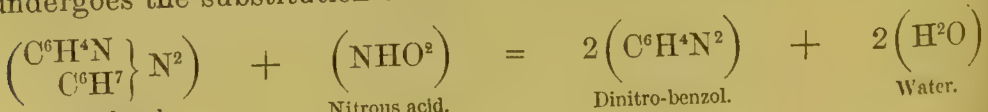
Ex.



$$2\left(C^6H^7N\right) + \left(NHO^2\right) = \left(\left.\begin{matrix}C^6H^4N^2\\C^6H^7N\end{matrix}\right\}\right) + 2\left(H^2O\right)$$

Aniline (phenylamine). Nitrous acid. Nitrophenyl-diamine. Water.

Under the influence of an excess of the nitrous acid, the new body undergoes the substitution of N for $H^3$ a second time:



$$\left(\left.\begin{matrix}C^6H^4N\\C^6H^7\end{matrix}\right\}N^2\right) + \left(NHO^2\right) = 2\left(C^6H^4N^2\right) + 2\left(H^2O\right)$$

Nitrophenyl-diamine. Nitrous acid. Dinitro-benzol. Water.

These compounds are obtained in the state of nitrates: those among them which are analogous to dinitro-benzol may be prepared not only by the action of nitrous acid on bodies which are analogous to dinitrophenyldiamine, being formed by the direct action of nitrous acid on the nitrates of the primary aromatic alkaloids dissolved in nitric acid and cooled.

$$\underset{\text{Phenylamine.}}{(C^6H^7N^2)} + \underset{\text{Nitrous acid.}}{(NHO^2)} = \underset{\text{Water.}}{2(H^2O)} + \underset{\text{Dinitro-benzol.}}{(C^6H^4N^2)}$$

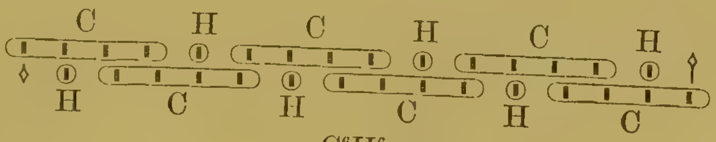
Boiled with water, dinitro-benzol and the analogous bodies lose nitrogen, and give rise to the hydrate of the radicle which existed in the alkaloid from which they are derived:

$$\underset{\text{Dinitro-benzol.}}{\left(C^6H^4N^2\right)} + \underset{\text{Water.}}{\left(H^2O\right)} = \underset{\substack{\text{Phenol}\\\text{(hydrate of phenyl).}}}{\left(\left.\begin{matrix}C^6H^5\\H\end{matrix}\right\}O\right)} + \underset{\text{Nitrogen.}}{N^2}$$

Treated with hydrochloric, hydrobromic, or hydriodic acid, they give rise to a chloride, bromide, or iodide of the radicle existing in the original alkaloid:

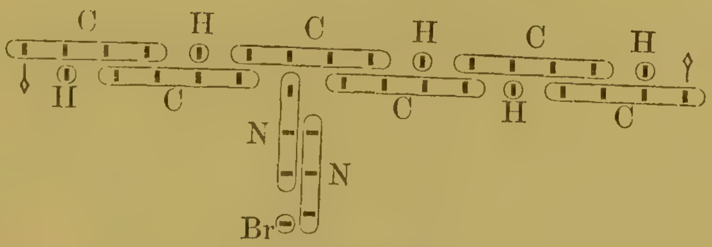
$$\underset{\text{Dinitro-benzol.}}{(C^6H^4N^2)} + \underset{\substack{\text{Hydrobromic}\\\text{acid.}}}{(HBr)} = \underset{\substack{\text{Bromide of}\\\text{phenyl.}}}{(C^6H^5Br)} + \underset{\text{Nitrogen.}}{N^2}$$

Griess, who discovered these compounds, admits that they are derived from the fundamental hydrocarbide of the series by the substitution of $N^2$ for $H^2$. Kékulé, on the other hand, regards them differently, on the ground that they can exist in a free state, which has not been demonstrated, as they have only been obtained in the state of salts.* He thinks that an atom of hydrogen in the fundamental hydrocarbide is saturated by one of the three atomicities of an atom of nitrogen (regarded as triatomic): the two remaining atomicities would be saturated by two atomicities of a second atom of nitrogen, and the atomicity which remains free in this second atom of nitrogen would be saturated by chlorine, bromine, or the halogen residue of nitric acid, as the following figures show:



$= C^6H^6$

Benzine.



$= (C^6H^4N^2HBr)$

Hydrobromate of dinitro-benzol.

The hypothesis of M. Kékulé explains the reactions of these bodies very well. To give an instance of this: when hydrobromic acid acts on them, the hydrobromate, of which the formula is given above, is first produced, then the nitrogen is separated in a free state and leaves the bromine, which unites with the carbon at the point previously occupied by nitrogen, and thus gives rise to the bromide of phenyl.

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* The product described as free dinitro-benzol has not been analyzed.

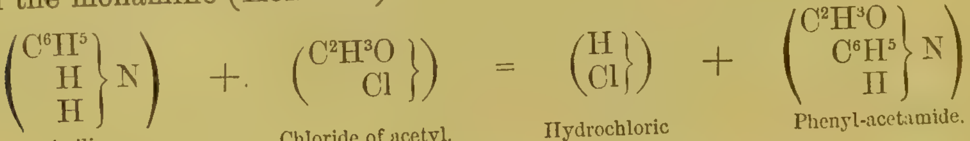
The action of nitrous acid on the ammonias of a more advanced degree of substitution is not yet known.

5th. Certain primary ammonias, belonging to the aromatic series, and obtained by Zinin's process (phenic ammonias), can, under the influence of chloride of carbon, chloride of tin, arsenic acid, pernitrate of mercury, nitro-benzine, and the chlorinating or oxidizing agents in general, produce new and much more complicated bases, the salts of which present very beautiful colours, and are successfully used for dyeing. This property has especially been observed in aniline and toluidine. Hofmann states that this character belongs exclusively to the mixture of the two bases and not to each one taken separately; but his opinion is contested.

6th. The hydrochlorates of the compound ammonias readily dissolve in absolute alcohol, a property which enables them to be separated from the chloride of ammonium, which is almost insoluble in that liquid.

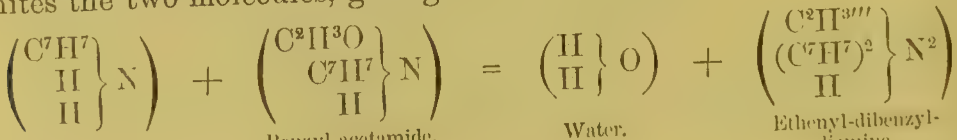
7th. With the bichloride of platinum, these hydrochlorates form double chlorides whose composition is analogous to that of the double chloride of platinum and ammonium. Sometimes these precipitates are scarcely soluble at all in the cold, sometimes they are more so; they always crystallize readily and are very useful for fixing the composition of the alkaloids, and enable us to judge of the purity of these products.

8th. When a primary aromatic monamine is submitted to the simultaneous action of acetic acid and phosphorous chloride, chloride of acetyl is first formed, which converts a portion of the alkaloid into an amide, containing the radicle acetyl and the radicle originally contained in the monamine (Hofmann).



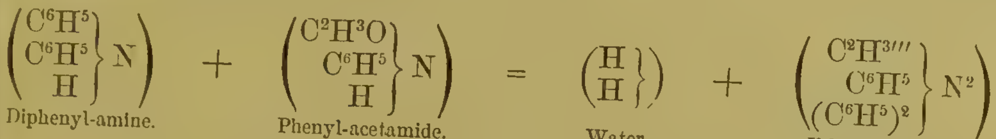
$$\underset{\text{Aniline.}}{\left(\left.\begin{matrix}C^6H^5\\H\\H\end{matrix}\right\}N\right)} + \underset{\text{Chloride of acetyl.}}{\left(\left.\begin{matrix}C^2H^3O\\Cl\end{matrix}\right\}\right)} = \underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Phenyl-acetamide.}}{\left(\left.\begin{matrix}C^2H^3O\\C^6H^5\\H\end{matrix}\right\}N\right)}$$

Phosphorous chloride then acts on the mixture of the undecomposed primary alkaloid and the amide formed in the first stage of the reaction. The elements of a molecule of water are eliminated; the oxygen is furnished by the acid radicle and one atom of H by a molecule of the monamine, the other being given by a molecule of the amide. The acid radicle deprived of O″ then becomes triatomic and unites the two molecules, giving rise to a diamine:



$$\underset{\text{Toluidine.}}{\left(\left.\begin{matrix}C^7H^7\\H\\H\end{matrix}\right\}N\right)} + \underset{\text{Benzyl-acetamide.}}{\left(\left.\begin{matrix}C^2H^3O\\C^7H^7\\H\end{matrix}\right\}N\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Ethenyl-dibenzyl-diamine.}}{\left(\left.\begin{matrix}C^2H^{3'''}\\(C^7H^7)^2\\H\end{matrix}\right\}N^2\right)}$$

Under the same conditions the secondary aromatic monamines undergo an analogous transformation, only the product no longer contains typical hydrogen.

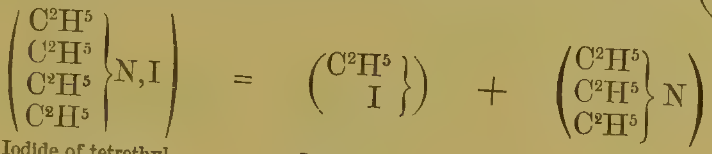


$$\left(\left.\begin{matrix}C^6H^5\\C^6H^5\\H\end{matrix}\right\}N\right)+\left(\left.\begin{matrix}C^2H^3O\\C^6H^5\\H\end{matrix}\right\}N\right)=\left(\left.\begin{matrix}H\\H\end{matrix}\right\}\right)+\left(\left.\begin{matrix}C^2H^{3'''}\\C^6H^5\\(C^6H^5)^2\end{matrix}\right\}N^2\right)$$

Diphenyl-amine. Phenyl-acetamide. Water. Ethenyl-triphenyl-diamine.

9th. The haloid salts of a compound ammonium $\left(\left.\begin{matrix}R^{n}\\H^{4-n}\end{matrix}\right\}N,x\right)$ ($x$ = Cl, Br or I) split up on distillation into a simple ether and a base $\left(\left.\begin{matrix}R^{n-1}\\H^{4-n}\end{matrix}\right\}N\right)$.

Ex.



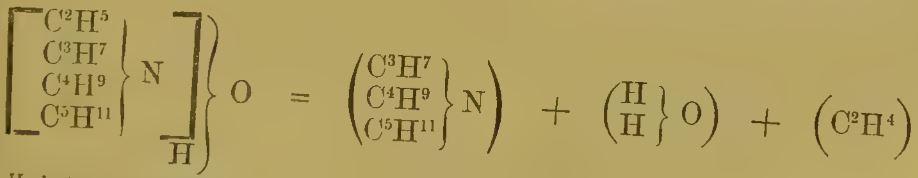
$$\left(\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right\}N,I\right)=\left(\left.\begin{matrix}C^2H^5\\I\end{matrix}\right\}\right)+\left(\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right\}N\right)$$

Iodide of tetrethyl-ammonium. Iodide of ethyl. Triethylamine.

Properties of the Hydrates of Quaternary Ammoniums.—1st. They are solid bodies which crystallize when their solutions are evaporated in vacuo. They are deliquescent, and attract moisture like caustic potash and soda.

2nd. They absorb carbonic anhydride directly.

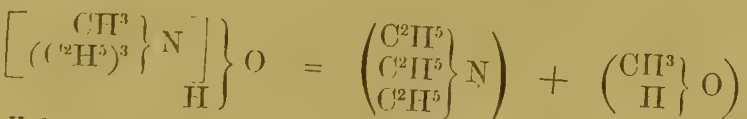
3rd. When distilled they decompose, producing a tertiary ammonia and water. A hydrocarbide is formed at the same time, derived from one of the four alcohol radicles by the elimination of H. When the hydrate decomposed contains several different alcohol radicles, it is always that which is the least carbonized which is separated from the group:



$$\left.\begin{matrix}\left[\left.\begin{matrix}C^2H^5\\C^3H^7\\C^4H^9\\C^5H^{11}\end{matrix}\right\}N\right]\\H\end{matrix}\right\}O=\left(\left.\begin{matrix}C^3H^7\\C^4H^9\\C^5H^{11}\end{matrix}\right\}N\right)+\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)+\left(C^2H^4\right)$$

Hydrate of ethyl-propyl-butyl-amyl-ammonium. Propyl-butyl-amylamine. Water. Ethylene.

There is, however, an exception to the above rule. When the hydrate contains methyl ($CH^3$), it is not separated as water and methylene, but as methylic alcohol:



$$\left.\begin{matrix}\left[\left.\begin{matrix}CH^3\\(C^2H^5)^3\end{matrix}\right\}N\right]\\H\end{matrix}\right\}O=\left(\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right\}N\right)+\left(\left.\begin{matrix}CH^3\\H\end{matrix}\right\}O\right)$$

Hydrate of triethyl-methyl-ammonium. Triethyl-amine. Methylic alcohol.

4th. Treated by the hydracids, the hydrates of ammoniums furnish haloid salts. Their chlorides give precipitates with the bichloride of platinum, or at least double salts which readily crystallize.

Nomenclature of the Compound Ammonias derived from Monatomic Alcohols.—The ammonias of the first three degrees, in the free state belong to the ammonia type; in the state of salts they belong to the ammonium type. It thence arises that each of them has two names, according as it exists free or combined.

If the ammonia be free, it is called an amine, and the name of the radicle substituted for the hydrogen is placed before this word. Then the syllables *mono*, *di*, *tri*, are prefixed to the name of this radicle to indicate its proportion in the compound; generally, *mono* is suppressed.

When there are different radicles present, the name of each is placed before the word *amine*, care being taken to put the syllable *di* before that one of which the compound ammonia contains two molecules, supposing there to be such a one.

Thus the compound $\left(\left.\begin{matrix}C^2H^5\\H\\H\end{matrix}\right\} N\right)$ is called ethylamine; the compound $\left(\left.\begin{matrix}C^3H^7\\C^3H^7\\H\end{matrix}\right\} N\right)$, dipropylamine; the compound $\left(\left.\begin{matrix}C^5H^{11}\\C^5H^{11}\\C^5H^{11}\end{matrix}\right\} N\right)$, triamylamine; the compound $\left(\left.\begin{matrix}CH^3\\C^2H^5\\C^6H^5\end{matrix}\right\} N\right)$, methyl-ethyl-phenylamine; the compound $\left(\left.\begin{matrix}CH^3\\CH^3\\C^5H^{11}\end{matrix}\right\} N\right)$, dimethyl-amylamine, etc.

When these bodies enter into saline combinations it is in the state of ammoniums. The names of these compounds are formed in the same manner as those of the amines whence they are derived, by simply substituting the word ammonium for amine. Thus, the chlorides of the ammoniums derived from the different ammonias we have given as examples would be the chlorides of ethyl-ammonium, dipropyl-ammonium, triamyl-ammonium, methyl-ethyl-phenyl-ammonium, and dimethyl-amyl-ammonium.

The quaternary ammoniums are named after the same rules. The body $\left(\left.\begin{array}{r}(C^2H^5)^4N\\H\end{array}\right\} O\right)$, for instance, would be the hydrate of tetrethyl-ammonium; the body $\left(\left.\begin{array}{r}(C^2H^5)^2(C^3H^7)^2N\\H\end{array}\right\} O\right)$ would be the hydrate of diethyl-dipropyl-ammonium; the body $\left(\left.\begin{array}{r}(CH^3)^3C^5H^{11}\\H\end{array}\right\} O\right)$ would be the hydrate of trimethyl-amyl-ammonium; the body

$$\left(\left.\begin{array}{r}CH^3,C^2H^5,C^4H^9,C^5H^{11},N\\H\end{array}\right\} O\right)$$

would be the hydrate of methyl-ethyl-butyl-amyl-ammonium.

*Appendix to the Monamines derived from Monatomic Alcohols.*

**Pseudo-Amylamine.**—Wurtz has obtained this by distilling the cyanic ether of amylic pseudo-alcohol with potash. Contrary to what might be expected considering the properties of the pseudo-alcohols, this base cannot be divided into ammonia and amylene. Wurtz explains this phenomenon in the following manner: the formula of amylic pseudo-alcohol is $\left(\left.\begin{matrix}[H,H^{10}C^5]'\\ H\end{matrix}\right\} O\right)$, and that of pseudo-amylamine is $\left(\left.\begin{matrix}[H,H^{10}C^5]'\\ H\\ H\end{matrix}\right\} N\right)$.

In both these bodies the pseudo-amyl is united by carbon in the one case to oxygen, in the other to nitrogen.

When the pseudo-alcohol is decomposed into water and amylene, the oxygen leaves the carbon and joins the hydrogen. For the pseudo-amylamine to be decomposed into amylene and ammonia, the nitrogen should separate from the carbon and go to the hydrogen. This does not take place, because carbon has a stronger affinity for nitrogen than for oxygen.

If this explanation be true, a cyanide ought to be formed when the pseudo-amylamine is decomposed by transmitting its vapour over red-hot baryta. Wurtz has found that cyanide of barium is formed under these conditions.

Though the differences which separate pseudo-amylamine from amylamine are not so marked as those which separate pseudo-alcohols from alcohols, these two bases are, nevertheless, isomers.

## AMINES DERIVED FROM BIATOMIC ALCOHOLS.

Any biatomic alcohol $\left(\left.\begin{matrix}R''\\ H^2\end{matrix}\right\} O^2\right)$ may lose its monatomic group (HO), vhen the residue $\left(\left.\begin{matrix}R''\\ H\end{matrix}\right\} O\right)$ has a tendency to become saturated, either y regaining the group (HO), or by uniting with any other monatomic adicle. It is monatomic, and may be substituted for one, two, three, our atoms of hydrogen in ammonium $(NH^4)$, or in ammonia $(NH^3)$. ence arise the monamines or monammoniums.

The biatomic alcohol may also lose twice the group (HO); the iatomic radicle R'' then remains. This latter may be substituted for ne, two, three, four times $H^2$ in the condensed ammonium or ammonia ypes. Thence arise the diamines and diammoniums. Thus there may xist monamines and monammoniums, resulting from the substitution R'' for $H^2$ in the simple types, but no body of this nature is known.

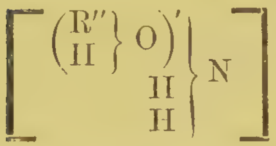
**Monamines derived from Biatomic Alcohols.**—Preparation.—

These compounds have been prepared for the first time by Wurtz. They may be obtained by two methods.

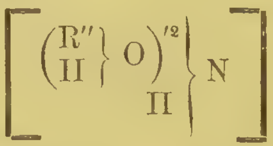
*First Process.*—The anhydride of a glycol is intimately mixed with a solution of ammonia: the reaction commences in the cold; the anhydride of the glycol combines directly with the ammonia. On saturating the compounds formed by hydrochloric acid, and separating the chlorides by fractional distillations, products are obtained the formulæ of which are:

$$(R''O,NH^3);([R''O]^2,NH^3);([R''O]^3,NH^3).$$

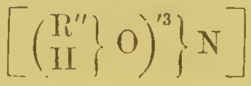
These bodies may be represented by the rational formulæ:



$$\left[\left.\begin{matrix}\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)'\\H\\H\end{matrix}\right\}N\right]$$



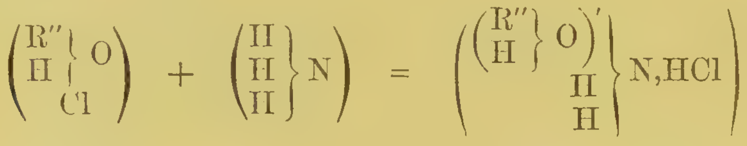
$$\left[\left.\begin{matrix}\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)'^2\\H\end{matrix}\right\}N\right]$$



$$\left[\left.\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)'^3\right\}N\right]$$

which indicate primary, secondary, and tertiary monamines arising from the substitution of the residue $\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)$ for hydrogen.

*Second Process.*—The chlorhydrin of a glycol is made to act on ammonia, then the ammonia formed is made to act on a second molecule of the chlorhydrin, and so on, as in Hofmann's process for the preparation of monamines of the monatomic alcohols:

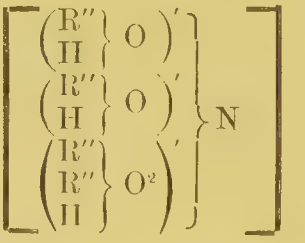


$$\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}\begin{matrix}O\\Cl\end{matrix}\right)+\left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right)=\left(\left.\begin{matrix}\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)'\\H\\H\end{matrix}\right\}N,HCl\right)$$

Chlorhydrin of a glycol. Ammonia. Hydrochlorate of a monamine derived from a glycol.

On submitting the tertiary monamine to the action either of chlorhydrin or of the anhydride of a glycol, a product is obtained the rough formula of which is $([R''O]^4,NH^3)$; in its turn this body can produce another $([R''O],^5NH^3)$; then another $([R''O]^6,NH^3)$; then another $([R''O)^7,NH^3)$, and so on.

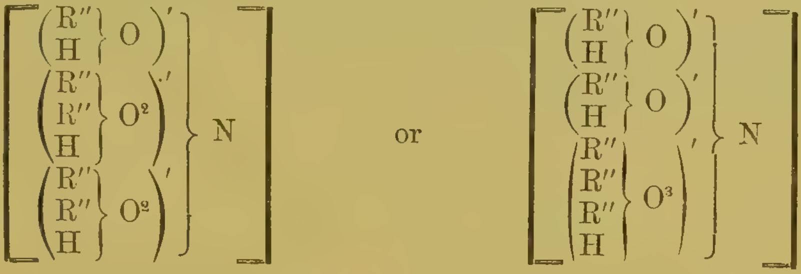
The constitution of these different compounds may be easily seen by admitting that the residues which are substituted for the hydrogen are derived by elimination of HO, not from a glycol, but from a condensed glycol. Thus the ammonia $([R''O]^4,NH^3]$ would have for rational formula:



$$\left[\left.\begin{matrix}\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)'\\\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)'\\\left(\left.\begin{matrix}R''\\R''\\H\end{matrix}\right\}O^2\right)'\end{matrix}\right\}N\right]$$

in which the third atom of hydrogen is replaced by the residue $\left(\left.\begin{matrix}R''\\R''\\H\end{matrix}\right\}O^2\right)$, derived from the condensed glycol $\left(\left.\begin{matrix}R''\\R''\\H^2\end{matrix}\right\}O^3\right)$ by the elimination of HO.

The compound $((RO)^5,NH^3)$ would have the formula:

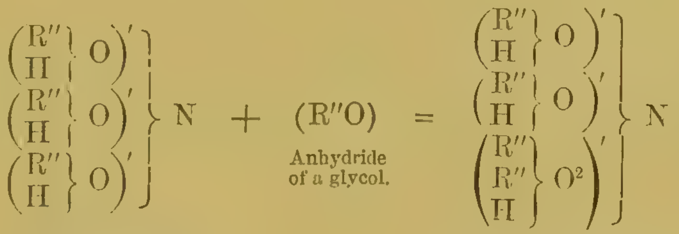


$$\left[\left.\begin{matrix}\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)'\\\left(\left.\begin{matrix}R''\\R''\\H\end{matrix}\right\}O^2\right)'\\\left(\left.\begin{matrix}R''\\R''\\H\end{matrix}\right\}O^2\right)'\end{matrix}\right\}N\right] \quad \text{or} \quad \left[\left.\begin{matrix}\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)'\\\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)'\\\left(\left.\begin{matrix}R''\\R''\\R''\\H\end{matrix}\right\}O^3\right)'\end{matrix}\right\}N\right]$$

In the first of these formulæ $H^2$ is supposed to be replaced by the residue $(R''^2HO^2)$ of the condensed glycol $\left(\left.\begin{matrix}R''^2\\H^2\end{matrix}\right\}O^3\right)$; in the second, $H^2$ is supposed to be replaced by the residue $(R''HO)$ of a simple glycol, and the third atom of H by the residue $(R''^3HO^3)$ of a glycol three times condensed $(R''^3H^2O^4)$. It would be difficult to decide between these two formulæ.

The derivatives which contain a greater number of atoms of the radicle of glycol would be represented by similar formulæ.

The following equations show how these bodies are formed, either by means of the anhydrides of biatomic alcohols, or by their chlorhydrins:

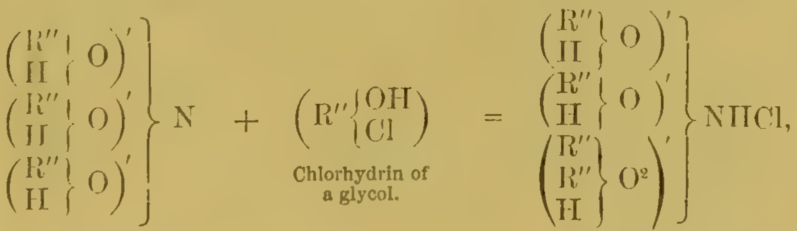


$$\left.\begin{matrix}\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)'\\\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)'\\\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)'\end{matrix}\right\}N + (R''O) = \left.\begin{matrix}\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)'\\\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)'\\\left(\left.\begin{matrix}R''\\R''\\H\end{matrix}\right\}O^2\right)'\end{matrix}\right\}N$$

Tertiary monamine containing three times the residue of a simple glycol.

Anhydride of a glycol.

Tertiary monamine containing twice the residue of a simple glycol, and once that of a condensed glycol.



$$\left.\begin{matrix}\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)'\\\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)'\\\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)'\end{matrix}\right\}N + \left(R''\left\{\begin{matrix}OH\\Cl\end{matrix}\right.\right) = \left.\begin{matrix}\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)'\\\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)'\\\left(\left.\begin{matrix}R''\\R''\\H\end{matrix}\right\}O^2\right)'\end{matrix}\right\}NHCl,$$

Tertiary monamine containing three times the residue of a simple glycol.

Chlorhydrin of a glycol.

Hydrochlorate of a tertiary monamine containing twice the residue of a simple glycol and once that of a condensed glycol.

*Properties.*—The properties of the different compound ammonias, the formation of which has just been indicated, are little known. They have,

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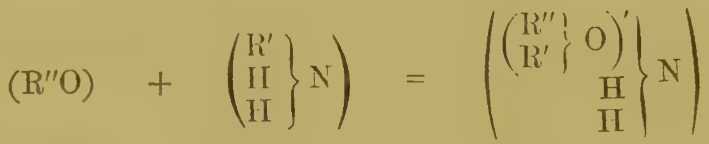
however, one fundamental property: the monatomic residues which are substituted for H always contain an atom of typical hydrogen. It is therefore evident that, whatever may be the number of these residues, the product, like ammonia, always contains three atoms of typical hydrogen which may be replaced by the radicles of monatomic alcohols.

Such bodies may therefore be obtained by causing, not ammonia, but the monamines of different degrees derived from monatomic alcohols to act on the anhydrides of the glycols:



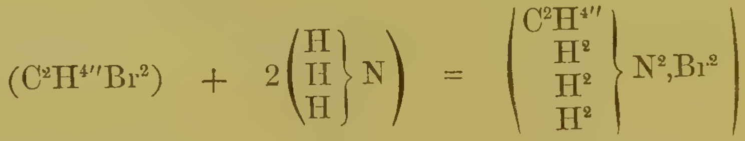
$$(R''O) \quad + \quad \left(\left.\begin{matrix}R'\\H\\H\end{matrix}\right\}N\right) \quad = \quad \left(\left.\begin{matrix}\left(\left.\begin{matrix}R''\\R'\end{matrix}\right\}O\right)\\H\\H\end{matrix}\right\}N\right)$$

Anhydride of a glycol.
Primary monamine.
Primary monamine derived from a glycol and an alcohol.

In fact, Wurtz has stated that aniline combines with the oxide of ethylene; he has not examined the products of the reaction.

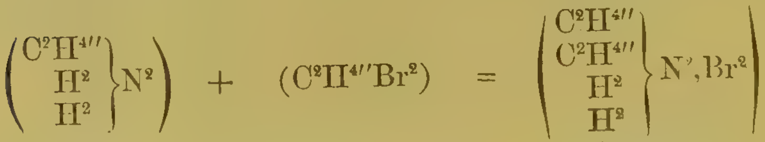
Another character of these bases is that they are oxygenized, not only in the free state as the hydrates of quaternary ammoniums derived from monatomic alcohols, but also in their hydrochlorates, hydrobromates, and hydriodates. In this character they approach the oxygenized alkaloids, which will be studied presently, and which are found ready formed in vegetables. It is possible that the natural alkaloids belong to this group, and that their synthesis may some day be accomplished. No satisfactory nomenclature has as yet been applied to the compound ammonias just spoken of.

**Diamines derived from Biatomic Alcohols.**—PREPARATION.—These bodies are obtained by causing ammonia to act on the bromides of biatomic hydrocarbon radicles; their mode of preparation is therefore similar to that of the monamines which are obtained by causing the simple ethers of monatomic alcohols to react with ammonia:



$$(C^2H^{4''}Br^2) \quad + \quad 2\left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right) \quad = \quad \left(\left.\begin{matrix}C^2H^{4''}\\H^2\\H^2\\H^2\end{matrix}\right\}N^2,Br^2\right)$$

Bromide of ethylene.
Ammonia.
Bromide of ethylene-diammonium.



$$\left(\left.\begin{matrix}C^2H^{4''}\\H^2\\H^2\end{matrix}\right\}N^2\right) \quad + \quad (C^2H^{4''}Br^2) \quad = \quad \left(\left.\begin{matrix}C^2H^{4''}\\C^2H^{4''}\\H^2\\H^2\end{matrix}\right\}N^2,Br^2\right)$$

Ethylene-diamine.
Bromide of ethylene.
Bromide of diethylene-diammonium.

*Properties.*—1st. These ammonias readily combine with a molecule of water, producing hydrates, which are decomposed by heat.

2nd. The primary diamines, submitted to the action of nitrous acid.

give nitrogen, water, and the anhydride of the glycol, the radicle of which they contain :

$$\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\H^2\\H^2\end{matrix}\right\}N^2\right) + 2\left(\left.\begin{matrix}NO'\\H\end{matrix}\right\}O\right) = 2\left(\left.\begin{matrix}N\\N\end{matrix}\right\}\right) + 3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + \left(C^2H^4O\right)$$

Ethylene-diamine. Nitrous acid. Nitrogen. Water. Oxide of ethylene.

3rd. When these bases still contain typical hydrogen,—ethyl, methyl, or any other monatomic radicle may be substituted for it. It appears, however, that it is always two atoms of hydrogen which are replaced by two molecules of a radicle, and that a single atom of hydrogen cannot be so replaced.

Thus the diethylic-diethylene diamine $\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\C^2H^{4\prime\prime}\\(C^2H^5)^2\end{matrix}\right\}N^2\right)$ is known, but not the monoethylic-diethylene diamene $\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\C^2H^{4\prime\prime}\\C^2H^5,H\end{matrix}\right\}N^2\right)$. It is, however, possible that this and other analogous bodies may be prepared.

4th. Combined with acids, these ammonias produce salts of diammoniums. These diammoniums are biatomic.

Thus we have :

$$([H^6(C^2H^{4\prime\prime})N^2]''I^2)$$

Iodide of ethylene-diammonium.

$$([H^4(C^2H^{4\prime\prime})^2N^2]I^2)$$

Iodide of diethylene-diammonium.

LEEDS SCHOOL OF MEDICINE

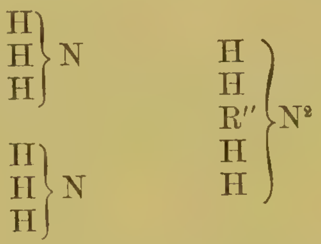
Nomenclature.—These bodies receive the names of diamines, or diammoniums, according as they are free and belong to the ammonia type, or combined and belong to the ammonium type. These names should follow that of the biatomic radicle substituted for $H^2$, this latter being preceded by the syllables, *di*, *tri*, etc., to indicate its number.

Thus we say ethylene-diamine, diethylene-diamine, triethylene-diamine, hydrated oxide of tetrethylene-diammonium.

When, besides the biatomic radicle, monatomic radicles enter into a diamine, the name formed according to the above rules follows that of the monatomic radicles which end in *ic* and are preceded by the syllables, *di*, *tri*, etc.

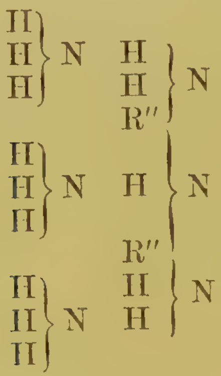
Thus the compound $\left.\begin{matrix}\left[\left.\begin{matrix}C^2H^{4\prime\prime}\\(C^2H^5)^2\\(C^2H^5)^2\\(C^2H^5)^2\end{matrix}\right\}N^2\right]\\H^2\end{matrix}\right\}O^2$ would take the name of hydrate of hexethylic-ethylene diammonium. If, instead of six atoms of the radicle ethyl, it contained four atoms of this radicle and two atoms of the methyl radicle, it would be called hydrate of dimethylic-tetrethylic-ethylene diammonium.

**Polyamines derived from Biatomic Alcohols.**—The formation of the diamines just spoken of is easily explained. If, in two molecules of ammonia, $H^2$ be replaced by an indivisible biatomic radicle, and the two atoms of H be each taken from a different molecule, the two molecules become united into one:



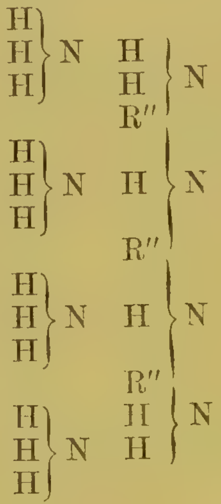
$$\begin{matrix}\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\\ \\ \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\end{matrix}\qquad\qquad \left.\begin{matrix}H\\H\\R''\\H\\H\end{matrix}\right\}N^2$$

From this explanation it will be understood that three, four . . . $n$ molecules of ammonia may be united by means of biatomic radicles, and that triamines, tetramines, etc., are thus produced:



$$\begin{array}{ll}\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N & \left.\begin{matrix}H\\H\\R''\end{matrix}\right\}N\\ \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N & \left.\begin{matrix}H\\ \\R''\end{matrix}\right\}N\\ \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N & \left.\begin{matrix}H\\H\end{matrix}\right\}N\end{array}$$

Triamine.



$$\begin{array}{ll}\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N & \left.\begin{matrix}H\\H\\R''\end{matrix}\right\}N\\ \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N & \left.\begin{matrix}H\\ \\R''\end{matrix}\right\}N\\ \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N & \left.\begin{matrix}H\\ \\R''\end{matrix}\right\}N\\ \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N & \left.\begin{matrix}H\\H\end{matrix}\right\}N\end{array}$$

Tetramine.

The formation of these polyamines by means of the bromides of biatomic radicles and ammonia, may be expressed by the general equation:

$$nR''Br^2 + 2nNH^3 = (R''^{n}H^{2n+4}N^{n+1})\,Br^{n+1} + n - 1NH^4Br.$$

If in this equation $n = 1$, which is the most simple case, diamines are produced. If $n$ be made equal to 2, triamines are obtained, and so on.

M. Hofmann has proved by experiment that this view is correct in the ethylenic series. The action of the bromide of ethylene on ammonia gives, besides the diamines of which we have spoken, the tribromide of diethylene-triammonium $\left(\left.\begin{matrix}(C^2H^{4''})^2\\H^8\end{matrix}\right\}N^3,Br^3\right)$ and the tribromide of triethylene-triammonium $\left(\left.\begin{matrix}(C^2H^{4''})^3\\H^6\end{matrix}\right\}N^3,Br^3\right)$

## COMPOUND AMMONIAS DERIVED FROM TRIATOMIC ALCOHOLS.

These bases have as yet been very little studied; theoretically their number may be very considerable, but they can only be separated from each other with great difficulty.

A glycerine $\left(\left.\begin{matrix}R'''\\H^3\end{matrix}\right\}O^3\right)$ may, on losing an atom of HO once, twice, or three times, give the residues $\left(\left.\begin{matrix}R'''\\H^2\end{matrix}\right\}O^2\right)'$, $\left(\left.\begin{matrix}R'''\\H\end{matrix}\right\}O\right)''$, or R'''. The first of these residues ought to be able to be substituted for one, two, or three atoms of the hydrogen of ammonia; also for the hydrogen of mono- or bi-atomic residues derived from glycerines by the elimination of HO or of 2HO.

The biatomic residue $\left(\left.\begin{matrix}R'''\\H\end{matrix}\right\}O\right)$ could be substituted for one, two, or three times $H^2$ in the condensed-type $\left.\begin{matrix}H^2\\H^2\\H^2\end{matrix}\right\}N^2$, giving rise to diamines; moreover, this residue, like the radicles of glycols, could give rise to triamines, tetramines, etc. It may also be conceived that it could replace the hydrogen of the biatomic radicles derived from polyglycerines by elimination of 2HO.

The radicle R''' could be substituted for $H^3$ once, twice, thrice, or four times, giving triammonic compounds. It is also evident that this radicle ought to be able to give rise to polyamines of a condensation higher than three.

Finally, from the polyglycerines containing more than three atoms of typical hydrogen, residues may be derived of an atomicity greater than three, which may also be substituted for the hydrogen of ammonia and produce polyamines.

Only two of all these probable compounds are known, glyceramine $\left(\left.\begin{matrix}\left(\left(\begin{matrix}C^3H^5\\H^2\end{matrix}\right)O^2\right)'\\H\\H\end{matrix}\right\}N\right)$, which Berthelot has obtained in the state of chlorhydrate by heating monochlorhydric glycerine with ammonia*, and a triamine obtained by Lautemann by submitting carbazotic acid (trinitrophenol) to the reducing action of hydriodic acid:

$$(C^6H^3(NO^2)^3O) + 23\left(\left.\begin{matrix}H\\I\end{matrix}\right\}\right) = \left(\left.\begin{matrix}C^6H^3\\H^3\\H^3\\H^3\end{matrix}\right\}N^3,I^3\right) + 7\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + 10\left(\left.\begin{matrix}I\\I\end{matrix}\right\}\right)$$

**Carbazotic acid. Hydriodic acid. Hydriodate of the new base. Water. Iodine.**

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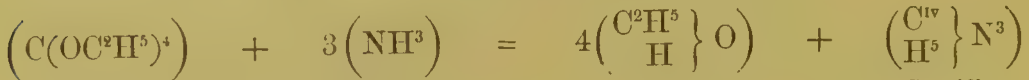
* Berthelot caused dichlorhydin and not monochlorhydrin to act on ammonia. But in a first stage of the reaction the ammonia transforms the dichlorhydrin into monochlorhydrin by an incomplete saponification.

## COMPOUND AMMONIAS DERIVED FROM ALCOHOLS OF A GREATER ATOMICITY THAN THREE.

On applying to these alcohols the considerations applied to bi- and tri-atomic alcohols, some idea may be obtained of the immense number of ammoniacal compounds to which they may give rise.

The polyamines of this order are little known. A base has been prepared which contains the radicle $C^{IV}$, guanidine $\left(\left.\begin{matrix}C^{IV}\\H^5\end{matrix}\right\}N^3\right)$ (*see* Guanine, Xanthine, Hypoxanthine), and one in which the radicle $(C^{10}H^4)$ is found, derived from naphthalin by the elimination of $H^4$. This latter has been prepared by the action of hydriodic acid on quadri-nitro-naphthalin. Hofmann has recently prepared guanidine by the action of ammonia on the orthocarbonate of ethyl:



$$\left(C(OC^2H^5)^4\right) + 3\left(NH^3\right) = 4\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}C^{IV}\\H^5\end{matrix}\right\}N^3\right)$$

Orthocarbonate of ethyl. Ammonia. Alcohol. Guanidine.

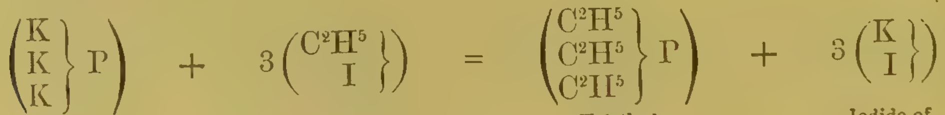
## PHOSPHURETTED, ARSENIURETTED, AND ANTIMONIURETTED AMMONIAS.

Phosphorus, arsenic, and antimony, belonging to the family of nitrogen, may be substituted for this metalloid. Hence the possibility of bases analogous to those just considered in which the nitrogen would be replaced by one of these three bodies.

In fact, compounds of this nature are known. But the primary and secondary phospuretted, arseniuretted, and antimoniuretted ammonias have not as yet been prepared.

Preparation of Phosphuretted and Arseniuretted Ammonias.— The tertiary phosphuretted and arseniuretted ammonias may be obtained by two processes:

*First Process.*—A hydrobromic or hydriodic ether is made to act on a phosphide or an arsenide.

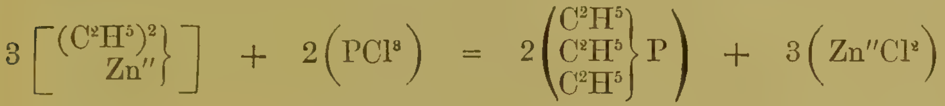


$$\left(\left.\begin{matrix}K\\K\\K\end{matrix}\right\}P\right) + 3\left(\left.\begin{matrix}C^2H^5\\I\end{matrix}\right\}\right) = \left(\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right\}P\right) + 3\left(\left.\begin{matrix}K\\I\end{matrix}\right\}\right)$$

Phosphide of potassium. Iodide of ethyl. Triethyl-phosphine. Iodide of potassium.

This process is well adapted for arseniuretted ammonias, but it is very little used for phosphuretted ammonias on account of the difficulty of preparing metallic phosphides.

*Second Process.*—The trichloride of phosphorus or arsenic is made to react with the compounds formed by zinc with alcohol radicles:



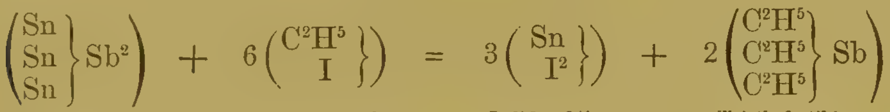
$$3\left[\left.\begin{matrix}(C^2H^5)^2\\ Zn''\end{matrix}\right\}\right] + 2\left(PCl^3\right) = 2\left(\left.\begin{matrix}C^2H^5\\ C^2H^5\\ C^2H^5\end{matrix}\right\}P\right) + 3\left(Zn''Cl^2\right)$$

Ethylide of zinc. Terchloride of phosphorus. Triethyl-phosphine. Chloride of zinc.

These reactions are generally accomplished very readily. The operation should always be conducted slowly, and the apparatus kept cool, owing to the violence with which the action takes place.

The second process is more convenient and sure than the first, but it is less general, as all the alcohol radicles have not been obtained combined with zinc.

PREPARATION OF ANTIMONIURETTED AMMONIAS.—These compounds are obtained by causing the simple ethers of monatomic alcohols to act on the antimonide of tin.



$$\left(\left.\begin{matrix}Sn\\ Sn\\ Sn\end{matrix}\right\}Sb^2\right) + 6\left(\left.\begin{matrix}C^2H^5\\ I\end{matrix}\right\}\right) = 3\left(\left.\begin{matrix}Sn\\ I^2\end{matrix}\right\}\right) + 2\left(\left.\begin{matrix}C^2H^5\\ C^2H^5\\ C^2H^5\end{matrix}\right\}Sb\right)$$

Antimonide of tin. Iodide of ethyl. Iodide of tin. Triethyl-stibine.

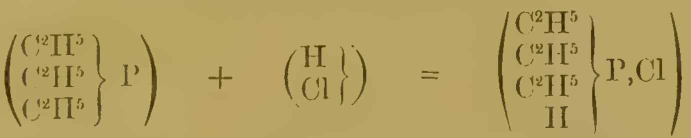
It is possible that these bodies might also be obtained by treating the terchloride of antimony by zinco-alcoholic compounds, but nothing of this kind has as yet been tried.

NOMENCLATURE.—The nomenclature of phosphuretted, arseniuretted, and antimoniuretted bases is the same as that of the ammonias proper. Only in the phosphorus series the word amine is replaced by *phosphine*; in the arsenic series it is replaced by the word *arsine*, and in that of antimony the word *stibine* is substituted.

Thus, the compounds $((C^2H^5)^3P)$, $((C^2H^5)^3As)$, and $((C^2H^5)^3Sb)$, are called triethyl-phosphine, triethyl-arsine, and triethyl-stibine.

The phosphuretted, antimoniuretted, or arseniuretted compounds of the ammonium type receive names analogous to those of the nitrogenized products of the same order, the word ammonium being replaced by the words phosphonium, arsonium, and stibium. Thus we should say: hydrated oxide of tetrethyl-phosphonium, iodide of tetramethyl-arsonium, etc.

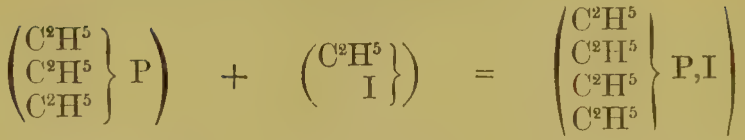
PROPERTIES OF THE PHOSPHINES.—1st. The different acids combine directly with the phosphines, giving salts of a tertiary phosphonium:



$$\left(\left.\begin{matrix}C^2H^5\\ C^2H^5\\ C^2H^5\end{matrix}\right\}P\right) + \left(\left.\begin{matrix}H\\ Cl\end{matrix}\right\}\right) = \left(\left.\begin{matrix}C^2H^5\\ C^2H^5\\ C^2H^5\\ H\end{matrix}\right\}P,Cl\right)$$

Triethyl-phosphine. Hydrochloric acid. Chloride of triethyl-phosphonium.

2nd. Phosphines combine directly with hydriodic ethers and give iodides of quaternary phosphoniums:



$$\left(\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right\}P\right) + \left(\left.\begin{matrix}C^2H^5\\I\end{matrix}\right\}\right) = \left(\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right\}P,I\right)$$

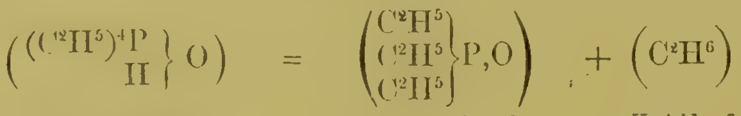
Triethyl-phosphine. Iodide of ethyl. Iodide of tetrethyl-phosphonium.

These iodides, submitted to the action of oxide of silver and water, give iodide of silver and the hydrate of the quaternary phosphonium of which they contain the elements.

3rd. Tertiary phosphines unite directly either with two atoms of chlorine, bromine, or iodine, or with one atom of oxygen, sulphur, selenium, or tellurium. Among the compounds thus formed the oxide is remarkable, as it acts as a basic anhydride capable of forming well-defined salts.

4th. When distilled, the hydrates of quaternary phosphoniums give the hydrides of their radicles, and the oxides of tertiary phosphines :

Ex.



$$\left(\left.\begin{matrix}(C^2H^5)^4P\\H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right\}P,O\right) + \left(C^2H^6\right)$$

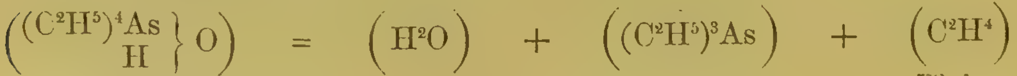
Hydrate of tetrethyl-phosphonium. Oxide of triethyl-phosphine. Hydride of ethyl.

PROPERTIES OF THE ARSINES.—1st. The arsines can in no case unite with hydracids to form salts ; they therefore in this respect do not act as true ammonias.

2nd. The arsines combine with the iodides of alcohol radicles, giving rise to iodides of quaternary arsoniums, which, with the oxide of silver and water, furnish the corresponding hydrates. These hydrates are bases equally as powerful as the hydrates of the corresponding ammoniums or phosphoniums.

3rd. The arsines are capable of uniting directly either with two atoms of chlorine, bromine, or iodine, or with one atom of oxygen, sulphur, selenium, or tellurium. The oxides act as basic anhydrides and give well-defined salts.

4th. The hydrates of quaternary arsoniums decompose by distillation like the hydrates of ammoniums, and not like the hydrates of phosphoniums. They give water, a tertiary arsine, and a hydrocarbide which differs from the radicle contained in the hydrate of arsonium by having H less :



$$\left(\left.\begin{matrix}(C^2H^5)^4As\\H\end{matrix}\right\}O\right) = \left(H^2O\right) + \left((C^2H^5)^3As\right) + \left(C^2H^4\right)$$

Hydrate of tetrethyl-arsonium. Water. Triethyl-arsine. Ethylene.

PROPERTIES OF STIBINES.—The stibines have properties which are similar to those of the arsines. But it is not yet known whether the hydrates of quaternary stibiums when heated split up like the hydrates of ammoniums and arsoniums, or like the hydrates of the phosphoniums.

The characters of the alcoholic derivatives of nitrogen, phosphorus, arsenic, and antimony establish between these four bodies greater analogies than can be deduced from the study of their mineral compounds.

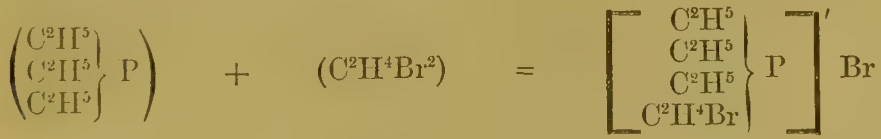
These bodies, by uniting with four radicles of monatomic alcohols, are all capable of furnishing complex radicles, the hydrates of which are powerful bases analogous to potash.

Moreover, in the compounds which are analogous to ammonia, gradual changes of properties are observed, as is the case in every well-established series. While ammonia is capable of uniting energetically with all the acids, phosphuretted hydrogen only possesses this property in the cases of hydrobromic and hydriodic acids, and neither arseniuretted nor antimoniuretted hydrogen possess it in any case. While the amines and tertiary phosphines both have great affinity for acids, arsines and stibines have none. The character of biatomic radicles observed in stibines, arsines, and phosphines is not observed in amines. It will be seen that phosphines are intermediate between amines on the one side, and arsines and stibines on the other. Like amines, they combine directly with acids; but, like arsines and stibines, they act as biatomic radicles.

## ACTION OF THE DIBROMHYDRIC ETHERS OF GLYCOLS ON THE DIFFERENT AMMONIAS HAVING MONATOMIC RADICLES.

These experiments have been made by Hofmann in the methylenic and ethylenic series. We will give the results obtained in the ethylenic series as example. It cannot be doubted that these results may be reproduced in the other series.

On causing the bromide of ethylene to act on a tertiary amine, phosphine, arsine, or stibine, Hofmann obtained in the state of bromides, ammoniums resulting from the addition of the radicle bromethyl ($C^2H^4Br$) to the ammonia employed:



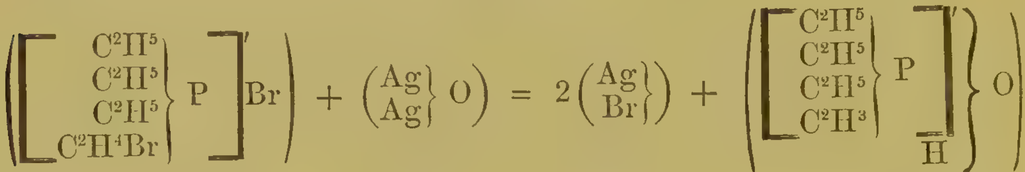
$$\left(\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right\}P\right) + (C^2H^4Br^2) = \left[\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\\C^2H^4Br\end{matrix}\right\}P\right]'Br$$

Triethyl-phosphine. Bromide of ethylene. Bromide of triethyl-bromethyl-phosphonium.

These salts contain the bromine in two different states. When they are treated with nitrate of silver, a single atom of bromine is precipitated.

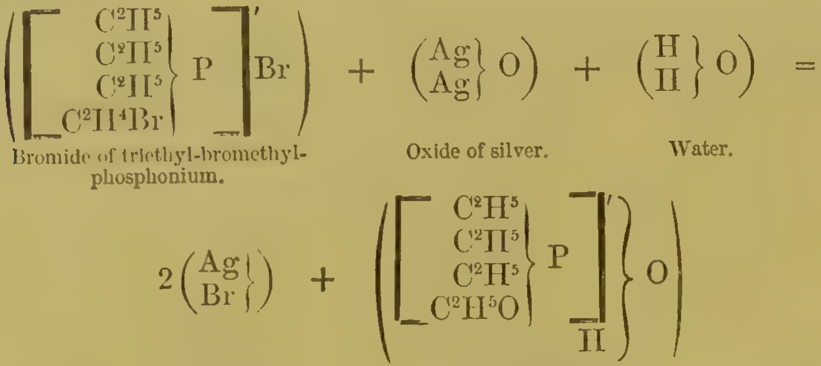
When heated with oxide of silver and water, according to the conditions under which the operation is conducted and which are not yet well determined, these bromides give rise to two different reactions.

Sometimes they lose an atom of bromine in the state of hydrobromic acid while the other atom is replaced by HO, when the hydrates of vinylic ammoniums, that is to say the ammoniums in which the fourth atom of hydrogen is replaced by the radicle vinyl ($C^2H^3$), are obtained. Sometimes the two atoms of bromine are replaced by two atoms of HO; we have then the hydrate of an oxethylic ammonium, that is to say, of an ammonium in which the fourth atom of hydrogen is replaced by the radicle oxethyl ($C^2H^5O$):



$$\left(\left[\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\\C^2H^4Br\end{matrix}\right\}P\right]'Br\right) + \left(\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}O\right) = 2\left(\left.\begin{matrix}Ag\\Br\end{matrix}\right\}\right) + \left(\left.\begin{matrix}\left[\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\\C^2H^3\end{matrix}\right\}P\right]'\\H\end{matrix}\right\}O\right)$$

Bromide of triethyl-bromethyl-phosphonium. Oxide of silver. Bromide of silver. Hydrate of triethyl-vinyl-phosphonium.



$$\left(\left[\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\\C^2H^4Br\end{matrix}\right\}P\right]'Br\right) + \left(\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) =$$

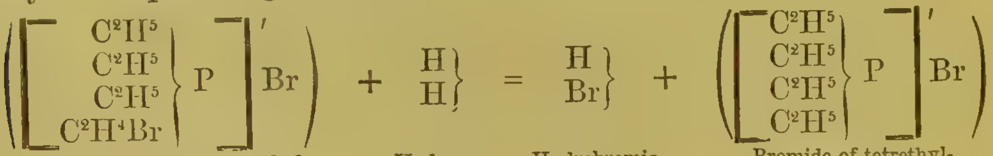
Bromide of triethyl-bromethyl-phosphonium. Oxide of silver. Water.

$$2\left(\left.\begin{matrix}Ag\\Br\end{matrix}\right\}\right) + \left(\left.\begin{matrix}\left[\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\\C^2H^5O\end{matrix}\right\}P\right]'\\H\end{matrix}\right\}O\right)$$

Bromide of silver. Hydrate of triethyl-oxethyl-phosphonium.

With the bromethylic bromides derived from the arsines, the first of these reactions takes place more easily than the second.

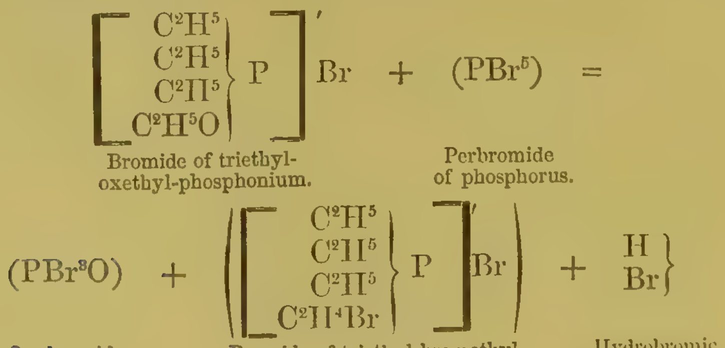
When these bromethylic compounds are treated by nascent hydrogen, this body is substituted for the bromine of the bromethyl, and a tetrethylic compound again arises:



$$\left(\left[\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\\C^2H^4Br\end{matrix}\right\}P\right]'Br\right) + \left.\begin{matrix}H\\H\end{matrix}\right\} = \left.\begin{matrix}H\\Br\end{matrix}\right\} + \left(\left[\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right\}P\right]'Br\right)$$

Bromide of triethyl-bromethyl-phosphonium. Hydrogen. Hydrobromic acid. Bromide of tetrethyl-phosphonium.

On submitting oxethylic bases to the action of the perbromide of phosphorus, the bromethylic compounds are re-formed:



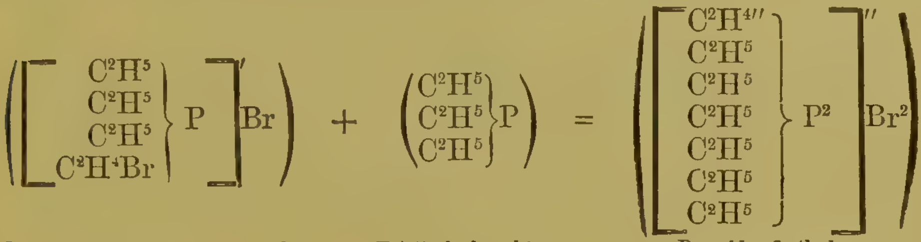
$$\left[\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\\C^2H^5O\end{matrix}\right\}P\right]'Br + (PBr^5) =$$

Bromide of triethyl-oxethyl-phosphonium. Perbromide of phosphorus.

$$(PBr^3O) + \left(\left[\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\\C^2H^4Br\end{matrix}\right\}P\right]'Br\right) + \left.\begin{matrix}H\\Br\end{matrix}\right\}$$

Oxybromide of phosphorus. Bromide of triethyl-bromethyl-phosphonium. Hydrobromic acid.

The bromethylic bromides obtained by means of phosphines, arsines, or stibines, may combine with a fresh molecule of the different tertiary ammonias, giving rise to bromides of biatomic ammoniums:



$$\left(\left[\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\\C^2H^4Br\end{matrix}\right\}P\right]'Br\right) + \left(\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right\}P\right) = \left(\left[\left.\begin{matrix}C^2H^{4\prime\prime}\\C^2H^5\\C^2H^5\\C^2H^5\\C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right\}P^2\right]''Br^2\right)$$

Bromide of triethyl-bromethyl-phosphonium. Triethyl-phosphine. Bromide of ethylene-hexethylic diphosphonium.

The bromethylic bromides derived from the amines do not combine with a second molecule of tertiary ammonia. But those bases which cannot be thus obtained may be easily procured by the action of the hydriodic ethers of monatomic alcohols on the primary diamines.

Thus the bromide of hexethylic ethylene-diammonium, corresponding to the bromide of hexethylic ethylene-diphosphonium, has been prepared by causing the iodide of ethyl to act on the ethylene diamine.

In the different reactions which have been mentioned, the bromides of the biatomic hydrocarbon radicles act like the bromides of the monobrominated monatomic radicles of the same series: the bromide of ethylene $(C^2H^{4\prime\prime}Br^2)$ acts like the bromide of brominated ethyl $(C^2H^4Br,Br)$. In fact, Hofmann is assured that exactly the same results are obtained when the bromide of brominated ethyl is substituted for the bromide of ethylene.

## COMPOUNDS OF ARSENIC WITH THE ALCOHOL RADICLES WHICH DO NOT CORRESPOND TO THE AMMONIA OR AMMONIUM TYPES.

It has been seen that nitrogen, phosphorus, arsenic, and antimony, on uniting with four radicles of alcohols, give rise to complex compounds which act as monatomic radicles, and which we have referred to the ammonium type, $NH^4$.—It has also been seen, that if the number of alcohol radicles united to these bodies is not more than three, the compounds formed act sometimes like ammonia, that is to say they unite directly with acids as is the case with amines and phosphines; and sometimes these compounds act as biatomic compound radicles, that is to say they unite with the elements, as is the case with phosphines, arsines, and stibines.

It may therefore be conceived that if compounds containing only two alcohol radicles, or one only of these radicles, could be obtained, these compounds would act as triatomic or tetratomic radicles.

Such compounds have not as yet been discovered in the nitrogen and antimony series, but some are known belonging to the phosphorus and arsenic series.

Those containing arsenic especially are well defined, and deserve our attention for a short time.

When a mixture of arsenious anhydride and acetate of potassium is distilled, a fuming liquid is obtained (Cadet's liquor), which contains arsenio-dimethyl or cacodyl $\left(\left.\begin{matrix}\mathrm{CH^3}\\ \mathrm{CH^3}\end{matrix}\right\}\mathrm{As}\right)$: this is placed in a flask full of carbonic anhydride to avoid combustion, washed with boiling water, and after it has been digested on fragments of potash it is distilled.

The distilled product, treated with the bichloride of mercury, gives a precipitate of the double chloride of mercury and cacodyl, which distillation with hydrochloric acid changes into chloride of cacodyl. This chloride, distilled with metallic zinc, abandons its chlorine to the metal, and the cacodyl liberated is disengaged in the form of vapours, which are condensed in a cold receiver full of carbonic anhydride.

Cacodyl thus prepared has the formula $\left(\begin{matrix}\mathrm{(CH^3)^2As}\\ \mathrm{(CH^3)^2As}\end{matrix}\right)$. It ignites spontaneously in the air, disengaging vapours of arsenious anhydride.

When oxygen is transmitted bubble by bubble into cacodyl, it first gives rise to protoxide of cacodyl $\left(\left.\begin{matrix}\mathrm{(CH^3)^2As}\\ \mathrm{(CH^3)^2As}\end{matrix}\right\}\mathrm{O}\right)$, then to a binoxide $\left(\left.\begin{matrix}\mathrm{(CH^3)^2As}\\ \mathrm{(CH^3)^2As}\end{matrix}\right\}\mathrm{O^2}\right)$, and finally to cacodylic acid $\left(\left.\begin{matrix}\mathrm{(CH^3)^2As}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O^2}\right)$.

Sulphur also combines directly with cacodyl, giving a protosulphide $\left(\left.\begin{matrix}\mathrm{(CH^3)^2As}\\ \mathrm{(CH^3)^2As}\end{matrix}\right\}\mathrm{S}\right)$ and a bisulphide $\left(\left.\begin{matrix}\mathrm{(CH^3)^2As}\\ \mathrm{(CH^3)^2As}\end{matrix}\right\}\mathrm{S^2}\right)$. Moreover, when hydrosulphuric acid is made to act on certain metallic cacodylates, sulpho-cacodylates $\left(\left.\begin{matrix}\mathrm{(CH^3)^2As}\\ \mathrm{M}\end{matrix}\right\}\mathrm{S^2}\right)$ are obtained.

Cacodyl also unites with chlorine, bromine, and iodine, forming compounds represented by the formulæ:

| $\mathrm{(CH^3)^2AsCl}$ | $\mathrm{(CH^3)^2AsBr}$ | $\mathrm{(CH^3)^2AsI}$ |
|---|---|---|
| Protochloride of cacodyl. | Protobromide of cacodyl. | Protiodide of cacodyl. |

With a great excess of oxygen, chlorine, bromine, sulphur, etc., cacodyl can also form the following compounds, which correspond to the grouping $X^5As$:

$$\begin{array}{l}\mathrm{(CH^3)^2As\ \ Cl^3}\\ \mathrm{(CH^3)^2As\ \ Br^3}\\ \mathrm{(CH^3)^2As\ \ I^3}\\ \left.\begin{matrix}\mathrm{(CH^3)^2As}\\ \mathrm{(CH^3)^2As}\end{matrix}\right\}\mathrm{O^3}\\ \left.\begin{matrix}\mathrm{(CH^3)^2As}\\ \mathrm{(CH^3)^2As}\end{matrix}\right\}\mathrm{S^3}\end{array}$$

These compounds, which are less stable than the preceding, easily return to the grouping $(AsX^3)$; thus the terchloride, terbromide, and teriodide of cacodyl, when submitted to distillation, lose a molecule of methyl in the state of chloride, bromide, or iodide, and bodies remain which have the formulæ ($CH^3As,Cl^2$), ($CH^3As,Br^2$), etc. These are the chloride, bromide, or iodide of a new radicle ($CH^3As$), which is tetratomic and cannot be isolated.

The chloride ($CH^3As,Cl^2$) and the bromide ($CH^3As,Br^2$), submitted to the influence of oxide of silver, give the oxide of cacodyl ($CH^3AsO$), together with bromide and chloride of silver. The oxide thus formed is an indifferent oxide.

Another oxide ($CH^3AsO^2$), which acts as a well-marked acid anhydride, is also obtained. The acid to which it gives rise should be tetrabasic, and have the formula $\left(\left.\begin{matrix}CH^3As\\ H^4\end{matrix}\right\}O^4\right)$; but only the first bibasic anhydride $\left(\left.\begin{matrix}CH^3As\\ H^2\end{matrix}\right\}O^3\right)$ is known.

The arsenio-monomethyl ($As(CH^3)$) can also unite with four atoms of chlorine, bromine, or iodine, giving the saturated compounds ($CH^3AsCl^4$), ($CH^3AsBr^4$), ($CH^3AsI^4$).

Cacodyl submitted to the action of the iodide of methyl gives iodide of cacodyl and iodide of tetramethyl-arsonium.

$$\underset{\text{Cacodyl.}}{\left(\left.\begin{matrix}(CH^3)^2As\\ (CH^3)^2As\end{matrix}\right\}\right)} + \underset{\text{Iodide of methyl.}}{2\left(\left.\begin{matrix}CH^3\\ I\end{matrix}\right\}\right)} = \underset{\text{Protiodide of cacodyl.}}{\left(\left.\begin{matrix}(CH^3)^2As\\ I\end{matrix}\right\}\right)} + \underset{\text{Iodide of tetramethyl-arsonium.}}{\left(\left.\begin{matrix}(CH^3)^4As\\ I\end{matrix}\right\}\right)}$$

This latter is resolved by distillation into iodide of methyl and trimethyl-arsine.

$$\underset{\text{Iodide of tetramethyl-arsonium.}}{\left(\left.\begin{matrix}(CH^3)^4As\\ I\end{matrix}\right\}\right)} = \underset{\text{Iodide of methyl.}}{\left(\left.\begin{matrix}CH^3\\ I\end{matrix}\right\}\right)} + \underset{\text{Trimethyl-arsine.}}{\left(\left.\begin{matrix}CH^3\\ CH^3\\ CH^3\end{matrix}\right\}As\right)}$$

Trimethyl-arsine may be readily prepared by means of this process. Its hydriodate splits up on distillation into iodide of methyl and cacodyl.

To sum up, compounds corresponding to the ammonium type and acting as monatomic radicles, may be easily obtained from arsenic and alcohol radicles.

If these bodies be submitted to dissociating influences, the alcohol radicle is separated in the state of chloride, bromide, or iodide, and less saturated compounds are obtained which act as radicles of an atomicity greater than one. Such are arsenio-monomethyl $[(CH^3)As]^{iv}$, which does not exist in the free state; cacodyl or arsenio-dimethyl $[(CH^3)^2As]'''$; triethylarsine $[(CH^3)^3As]''$, and tetramethyl arsonium $[(CH^3)^4As]$: as yet the saturated compound ($(CH^3)^5As$) has not been obtained in a pure state, but the results of analysis render the production of this body very probable by the action of zinc-methyl on the iodide of tetramethyl arsonium:

$$\underset{\text{Iodide of tetramethyl-arsonium.}}{2\left(\left.\begin{matrix}(CH^3)^4As\\ I\end{matrix}\right\}\right)} + \underset{\text{Zinc-methyl.}}{\left(\left.\begin{matrix}Zn''\\ (CH^3)^2\end{matrix}\right\}\right)} = \underset{\text{Iodide of zinc.}}{\left(\left.\begin{matrix}Zn''\\ I^2\end{matrix}\right\}\right)} + \underset{\text{Arsenio-pentamethyl.}}{2\left((CH^3)^5As\right)}$$

Commencing with triethyl-arsine, a whole series of ethyl compounds have been prepared resembling the preceding, from which they only differ by the substitution of the radicle ethyl for the radicle methyl.

It is extremely probable that similar series could be obtained with antimony and phosphorus.

## ORGANO-METALLIC COMPOUNDS.

We formerly studied, under the title of compound ammonias, bodies formed by the combination of metalloids of the nitrogen class with alcohol radicles, and which belong to the ammonia or ammonium types.

We then saw that arsenic, phosphorus, and probably antimony give, with alcohol radicles, compounds which do not belong to those types.

These arsenical compounds are intermediate between the compound ammonias and the combinations of the radicles of alcohols with elements which do not belong to the nitrogen family. These latter compounds are called organo-metallic.

Each element having a maximum atomicity, can form with alcohol radicles, a saturated compound which corresponds to this atomicity. It can also form compounds containing the alcohol radicles in smaller proportion: these themselves act as radicles, and their atomicity is equal to the number of molecules of the radicle of alcohol which must be added to them in order to obtain a saturated compound.

As little can be added to these general remarks on organo-metallic compounds, we will rapidly pass in review the principal among them.

**Ethylides of Bismuth.**—As bismuth is intermediate between the metalloids of the nitrogen family and the other elements, the compounds it forms with the radicles of alcohols differ entirely in their properties from the ammonias. These are compound radicles like the similar bodies derived from arsenic, but they are not capable of giving rise to quaternary ammoniums.

Two ethylides of bismuth are known: bismuth ethyl $(Bi(C^2H^5))$ and bismuth triethyl $(Bi(C^2H^5)^3)$. Either of them can fix two atoms of a monatomic body or an equivalent quantity of another body: they then pass to the groupings $(BiX^3)$ or $(BiX^5)$.

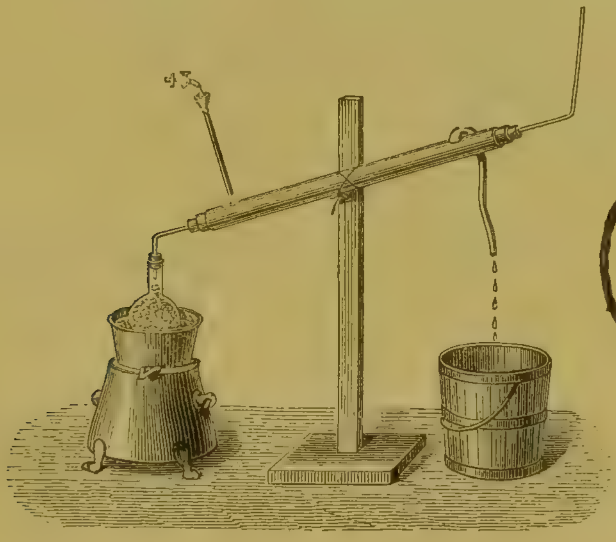
Methylides of bismuth are also known which possess similar formulæ and properties.

The ethylides and methylides of bismuth are extremely instable.

**Ethylide, Methylide, and Amylide of Zinc.**—The ethylide of zinc, or zinc-ethyl, may be obtained by heating a mixture of iodide of ethyl and zinc in a hermetically-sealed tube for fifteen or twenty hours at

120° or 130°. The tube is then opened, and the contents are distilled in a retort into which a current of carbonic anhydride is transmitted. The zinc-ethyl passes over at 118°.

Recently, Beilstein has simplified the preparation of this body by substituting an alloy of zinc and sodium for zinc. He introduces the mixture of iodide of ethyl and this alloy into a flask, to which a refrigerator is adapted in such a manner that the vapours are collected and condensed as they form. The flask is heated for two hours at 60°—70° in a water-bath, and afterwards the contents are distilled in a bath of oil. The apparatus is represented in figure 51.



LEEDS SCHOOL OF MEDICINE

Fig. 51.

The formula of zinc-ethyl is $\left(Zn''\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right.\right)$. It ignites in the air, producing oxide of zinc. Chlorine, bromine, and iodine decompose it, forming separate chlorides, bromides, or iodides of zinc and of ethyl.

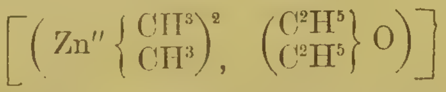
When oxygen acts slowly on zinc-ethyl, it transforms it into a crystallized product whose formula is $\left(\left.\begin{matrix}Zn''\\(C^2H^5)^2\end{matrix}\right\}O^2\right)$; it is the ethylate of zinc corresponding to the hydrate $\left(\left.\begin{matrix}Zn''\\H^2\end{matrix}\right\}O^2\right)$, the hydrogen of which is replaced by ethyl. This ethylate, on contact with water, is transformed into hydrate of zinc and alcohol:

$$\underset{\text{Ethylate of zinc.}}{\left(\left.\begin{matrix}Zn''\\(C^2H^5)^2\end{matrix}\right\}O^2\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Hydrate of zinc.}}{\left(\left.\begin{matrix}Zn''\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Alcohol.}}{2\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)}$$

Water instantly decomposes zinc-ethyl, producing hydrate of zinc and hydride of ethyl:

$$\underset{\text{Zinc-ethyl.}}{\left(\left.\begin{matrix}Zn''\\(C^2H^5)^2\end{matrix}\right\}\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Hydrate of zinc.}}{\left(\left.\begin{matrix}Zn''\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Hydride of ethyl.}}{2\left(C^2H^6\right)}$$

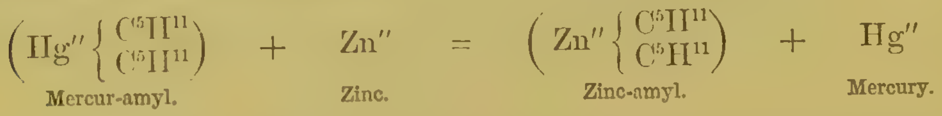
Zinc-methyl ($Zn''(CH^3)^2$) may be obtained by a process identical with the first which was described for the preparation of zinc-ethyl, the iodide of ethyl being replaced by the iodide of methyl. An ethereal solution of this latter body is generally employed. The product obtained is not pure zinc-methyl, but a combination of zinc-methyl and ether, having the formula:



$$\left[\left(Zn''\begin{cases}CH^3\\CH^3\end{cases}\right)^2, \left(\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\} O\right)\right]$$

Zinc-methyl gives rise to a series of double decompositions similar to those we mentioned when speaking of zinc-ethyl.

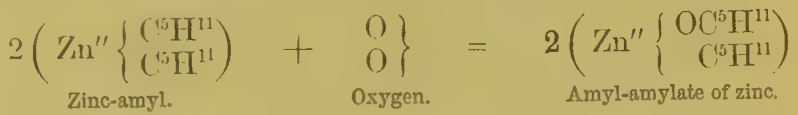
Zinc-amyl is obtained by heating a mixture of powdered zinc and mercur-amyl in a closed vessel at 130° during thirty-six hours.



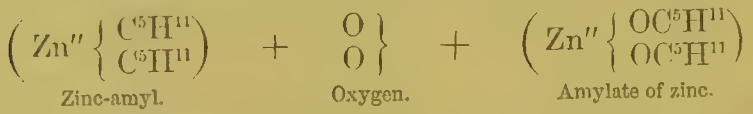
$$\underset{\text{Mercur-amyl.}}{\left(Hg''\begin{cases}C^5H^{11}\\C^5H^{11}\end{cases}\right)} + \underset{\text{Zinc.}}{Zn''} = \underset{\text{Zinc-amyl.}}{\left(Zn''\begin{cases}C^5H^{11}\\C^5H^{11}\end{cases}\right)} + \underset{\text{Mercury.}}{Hg''}$$

It is a colourless, limpid, volatile liquid, having an odour of amyl. Its density is 1·022 at 0°. It boils without decomposing at 220°, and is destroyed at 240°.

It oxidizes in the air, and is transformed successively into amyl-amylate and then into amylate of zinc:



$$2\underset{\text{Zinc-amyl.}}{\left(Zn''\begin{cases}C^5H^{11}\\C^5H^{11}\end{cases}\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} = 2\underset{\text{Amyl-amylate of zinc.}}{\left(Zn''\begin{cases}OC^5H^{11}\\C^5H^{11}\end{cases}\right)}$$

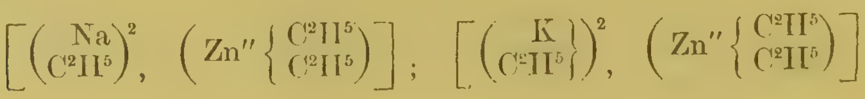


$$\underset{\text{Zinc-amyl.}}{\left(Zn''\begin{cases}C^5H^{11}\\C^5H^{11}\end{cases}\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} + \underset{\text{Amylate of zinc.}}{\left(Zn''\begin{cases}OC^5H^{11}\\OC^5H^{11}\end{cases}\right)}$$

Zinc-ethyl and zinc-methyl may also be prepared by the same process as zinc-amyl, that is to say, by heating zinc with mercur-ethyl or mercur-methyl.

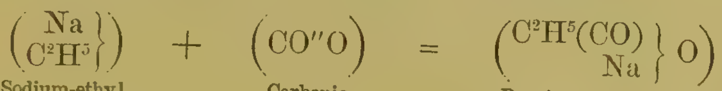
Zinc-methyl, zinc-ethyl, and zinc-amyl are valuable reagents, as they enable us to fix methyl, ethyl, and amyl in organic molecules: we have seen examples of this in the preparation of triethyl-phosphine and trimethyl-phosphine, and in the synthesis of amylene.

**Potassium-ethyl and Sodium-ethyl.**—These bodies are obtained by leaving mixtures of zinc-ethyl and potassium, and of zinc-ethyl and sodium, for some time in hermetically-sealed tubes. Zinc is deposited, and potassium-ethyl or sodium-ethyl is produced. They are never obtained in an isolated state. The products which form are only combinations of potassium-ethyl or sodium-ethyl with zinc-ethyl. These compounds are crystallizable; their composition is represented by the formulæ:



$$\left[\left(\begin{matrix}Na\\C^2H^5\end{matrix}\right)^2, \left(Zn''\begin{cases}C^2H^5\\C^2H^5\end{cases}\right)\right]; \left[\left(\left.\begin{matrix}K\\C^2H^5\end{matrix}\right\}\right)^2, \left(Zn''\begin{cases}C^2H^5\\C^2H^5\end{cases}\right)\right]$$

Sodium-ethyl and potassium-ethyl ignite in the air. Their most remarkable property is the faculty they possess of absorbing carbonic anhydride and giving rise to an alkaline propionate :

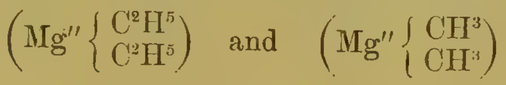


$$\left(\left.\begin{matrix}\mathrm{Na}\\ \mathrm{C^2H^5}\end{matrix}\right\}\right) + \left(\mathrm{CO''O}\right) = \left(\left.\begin{matrix}\mathrm{C^2H^5(CO)}\\ \mathrm{Na}\end{matrix}\right\}\mathrm{O}\right)$$

Sodium-ethyl. Carbonic anhydride. Propionate of sodium.

With potassium and sodium, methyl gives compounds analogous to those furnished by ethyl. By the direct union of potassium-methyl with carbonic anhydride, acetate of potassium is produced.

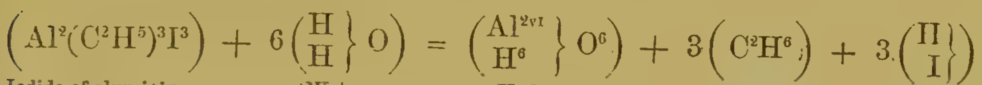
**Ethylide and Methylide of Magnesium.**—Powdered magnesium acts on the iodides of ethyl and methyl, producing ethylide and methylide of magnesium, the formulæ of which are :



$$\left(\mathrm{Mg''}\left\{\begin{matrix}\mathrm{C^2H^5}\\ \mathrm{C^2H^5}\end{matrix}\right.\right) \text{ and } \left(\mathrm{Mg''}\left\{\begin{matrix}\mathrm{CH^3}\\ \mathrm{CH^3}\end{matrix}\right.\right)$$

They have properties analogous to those of zinc-ethyl and zinc-methyl.

**Ethylide and Methylide of Aluminium.**—On heating to 130° for 24 hours a mixture of iodide of ethyl and aluminium, a liquid is obtained which is volatile at 350°, the formula of which is $(\mathrm{Al^2(C^2H^5)^3I^3})$. This body ignites in the air, and decomposes water, producing hydrate of aluminium, hydriodic acid, and probably hydride of ethyl :



$$\left(\mathrm{Al^2(C^2H^5)^3I^3}\right) + 6\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right) = \left(\left.\begin{matrix}\mathrm{Al^{2vi}}\\ \mathrm{H^6}\end{matrix}\right\}\mathrm{O^6}\right) + 3\left(\mathrm{C^2H^6}\right) + 3\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{I}\end{matrix}\right\}\right)$$

Iodide of aluminium-triethyl. Water. Hydrate of aluminium. Hydride of ethyl. Hydriodic acid.

Recently, Odling and Buckton have obtained aluminium-ethyl and aluminium-methyl by heating mercur-ethyl or mercur-methyl, with sheets of aluminium, in a water bath for several hours. Contrary to what might be expected, these two bodies present vapour densities which give them the formulæ $(\mathrm{Al(C^2H^5)^3})$ and $(\mathrm{Al(CH^3)^3})$ instead of $(\mathrm{Al^2(C^2H^5)^6})$ and $(\mathrm{Al^2(CH^3)^6})$.

Aluminium-ethyl is a colourless volatile liquid, which is not modified at 18°. Exposed to the air, it emits opaque fumes, and even ignites spontaneously if in a thin layer. Its vapour density, determined at 234° by Gay-Lussac's process, has been found to be 4·5 ; its theoretical density according to the formula $(\mathrm{Al(C^2H^5)^3})$ being 3·9, and that for the formula $(\mathrm{Al^2(C^2H^5)^6})$ being 7·8. Water decomposes it with violence ; iodine transforms it into iodide of ethyl and iodized derivatives.

Aluminium-methyl boils at 130° and is solidified at a few degrees above 0 ; its chemical properties are the same as those of aluminium-ethyl. Its vapour density at 240° is 2·8, its theoretical density, according to the formula $(\mathrm{Al(CH^3)^3})$, being 2·5 ; at 160° its vapour density is 4·40, which number approaches the theoretical density 5·0 calculated according to the formula $(\mathrm{Al^2(CH^3)^6})$. Aluminium-methyl therefore belongs to that class of bodies whose vapour densities are anomalous under certain conditions, either because these bodies exist in two states of molecular condensation or because their vapours do not acquire their perfect elasticity except when brought to a much higher temperature than the boiling points of their liquids, or else because they are dissociated above a certain temperature. It may therefore be asked, whether the only observed vapour density of aluminic chloride corresponds to the high density of aluminium-methyl, and whether these two vapour densities are not anomalous, and consequently unfit to serve as basis for determining the general formulæ of aluminic compounds.

**Stannides of Ethyl and Methyl.**—Tin is a tetratomic body, and ought therefore to be able to unite at the maximum with four atoms of the radicles ethyl or methyl to form saturated compounds. Moreover, it may be supposed that tin can combine with three, two, or one atom of an alcohol radicle, and thus give non-saturated compounds acting as radicles of an atomicity equal to the number of atoms of ethyl or methyl which they require for their saturation.

We should thus have:

Tetrastannethyl and tetrastanmethyl $\left(\left.\begin{matrix}\mathrm{Sn^{IV}}\\(\mathrm{C^2H^5})^4\end{matrix}\right\}\right)$ and $\left(\left.\begin{matrix}\mathrm{Sn^{IV}}\\(\mathrm{CH^3})^4\end{matrix}\right\}\right)$; tristannethyl and tristanmethyl $\left(\left.\begin{matrix}\mathrm{Sn^{IV}}\\(\mathrm{C^2H^5})^3\end{matrix}\right\}\right)'$ and $\left(\left.\begin{matrix}\mathrm{Sn^{IV}}\\(\mathrm{CH^3})^3\end{matrix}\right\}\right)'$, both monatomic radicles;

Distannethyl and distanmethy $\left(\left.\begin{matrix}\mathrm{Sn^{IV}}\\(\mathrm{C^2H^5})^2\end{matrix}\right\}\right)''$ and $\left(\begin{matrix}\mathrm{Sn^{IV}}\\(\mathrm{CH^3})^2\end{matrix}\right)''$, both biatomic radicles;

Monostannethyl and monostanmethyl $\left(\left.\begin{matrix}\mathrm{Sn^{IV}}\\\mathrm{C^2H^5}\end{matrix}\right\}\right)'''$ and $\left(\left.\begin{matrix}\mathrm{Sn^{IV}}\\\mathrm{CH^3}\end{matrix}\right\}\right)'''$, both being triatomic radicles.

With the exception of monostannethyl and monostanmethyl, all these compounds are known; those among them which have an uneven atomicity correspond when free to formulæ double the preceding.

When iodide of ethyl is heated with an alloy of zinc and sodium, in which the alkaline metal largely predominates, care being taken that there be a great excess of the alloy, all the iodine unites with the sodium, and three liquids are obtained which can be separated by fractional distillation, and which are:

Tetrastannethyl $(\mathrm{Sn(C^2H^5)^4})$.

**Free tristannethyl** $\left(\left.\begin{matrix}\mathrm{Sn(C^2H^5)^3}\\\mathrm{Sn(C^2H^5)^3}\end{matrix}\right\}\right)$.

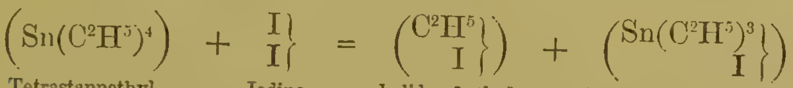
Distannethyl $(\mathrm{Sn(C^2H^5)^2})$.

If iodine be made to act on tristannethyl, an oily iodide of this radicle is obtained:

$$\underset{\text{Tristannethyl.}}{\left(\left.\begin{matrix}\mathrm{Sn(C^2H^5)^3}\\\mathrm{Sn(C^2H^5)^3}\end{matrix}\right\}\right)} + \underset{\text{Iodine.}}{\left.\begin{matrix}\mathrm{I}\\\mathrm{I}\end{matrix}\right\}} = \underset{\text{Iodide of tristannethyl.}}{2\left(\left.\begin{matrix}\mathrm{Sn(C^2H^5)^3}\\\mathrm{I}\end{matrix}\right\}\right)}$$

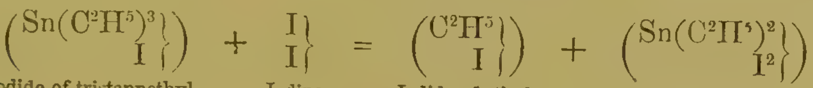
With distannethyl, iodine produces a crystallized biniodide, the formula of which is $(\mathrm{Sn(C^2H^5)^2I^2})$.

Tetrastannethyl, on the contrary, is incapable of combining directly with iodine. When a mixture of these two bodies is heated, a molecule of ethyl is eliminated in the state of iodide, and iodine is substituted for it. The iodide of tristannethyl is thereby obtained:



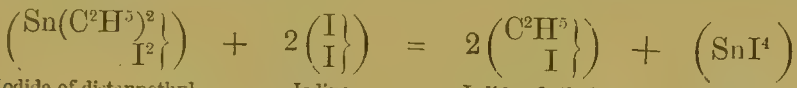
$$\underset{\text{Tetrastannethyl.}}{\left(\mathrm{Sn(C^2H^5)^4}\right)} + \underset{\text{Iodine.}}{\left.\begin{matrix}\mathrm{I}\\ \mathrm{I}\end{matrix}\right\}} = \underset{\text{Iodide of ethyl.}}{\left(\left.\begin{matrix}\mathrm{C^2H^5}\\ \mathrm{I}\end{matrix}\right\}\right)} + \underset{\text{Iodide of tristannethyl.}}{\left(\left.\begin{matrix}\mathrm{Sn(C^2H^5)^3}\\ \mathrm{I}\end{matrix}\right\}\right)}$$

The iodide of tristannethyl, heated with iodine, again loses a molecule of ethyl, for which an atom of iodine is substituted, giving rise to the iodide of distannethyl:



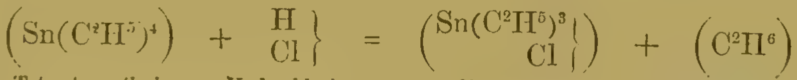
$$\underset{\text{Iodide of tristannethyl.}}{\left(\left.\begin{matrix}\mathrm{Sn(C^2H^5)^3}\\ \mathrm{I}\end{matrix}\right\}\right)} + \underset{\text{Iodine.}}{\left.\begin{matrix}\mathrm{I}\\ \mathrm{I}\end{matrix}\right\}} = \underset{\text{Iodide of ethyl.}}{\left(\left.\begin{matrix}\mathrm{C^2H^5}\\ \mathrm{I}\end{matrix}\right\}\right)} + \underset{\text{Binioidide of distannethyl.}}{\left(\left.\begin{matrix}\mathrm{Sn(C^2H^5)^2}\\ \mathrm{I^2}\end{matrix}\right\}\right)}$$

Lastly, this iodide of distannethyl, heated with iodine, is transformed into iodide of ethyl and iodide of tin:

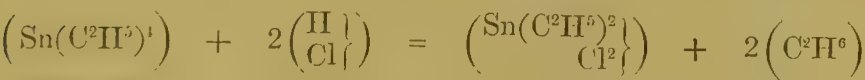


$$\underset{\text{Iodide of distannethyl.}}{\left(\left.\begin{matrix}\mathrm{Sn(C^2H^5)^2}\\ \mathrm{I^2}\end{matrix}\right\}\right)} + \underset{\text{Iodine.}}{2\left(\left.\begin{matrix}\mathrm{I}\\ \mathrm{I}\end{matrix}\right\}\right)} = \underset{\text{Iodide of ethyl.}}{2\left(\left.\begin{matrix}\mathrm{C^2H^5}\\ \mathrm{I}\end{matrix}\right\}\right)} + \underset{\text{Stannic iodide.}}{\left(\mathrm{SnI^4}\right)}$$

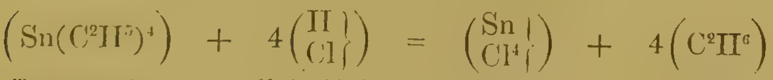
Similar results are obtained with hydrochloric acid. If quantities of this acid and tetrastannethyl respectively proportional to their molecular weights, be heated together, chloride of tristannethyl and hydride of ethyl are obtained. If a double or quadruple proportion of hydrochloric acid be made to act on the tetrastannethyl, twice or four times the quantity of ethyl is eliminated in the state of hydride, and there finally remain chloride of distannethyl and tetrachloride of tin respectively:



$$\underset{\text{Tetrastannethyl.}}{\left(\mathrm{Sn(C^2H^5)^4}\right)} + \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}\mathrm{H}\\ \mathrm{Cl}\end{matrix}\right\}} = \underset{\text{Chloride of tristannethyl.}}{\left(\left.\begin{matrix}\mathrm{Sn(C^2H^5)^3}\\ \mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\text{Hydride of ethyl.}}{\left(\mathrm{C^2H^6}\right)}$$

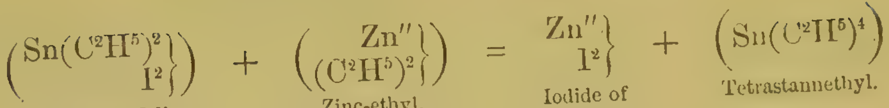


$$\underset{\text{Tetrastannethyl.}}{\left(\mathrm{Sn(C^2H^5)^4}\right)} + \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{Cl}\end{matrix}\right\}\right)} = \underset{\text{Chloride of distannethyl.}}{\left(\left.\begin{matrix}\mathrm{Sn(C^2H^5)^2}\\ \mathrm{Cl^2}\end{matrix}\right\}\right)} + \underset{\text{Hydride of ethyl.}}{2\left(\mathrm{C^2H^6}\right)}$$



$$\underset{\text{Tetrastannethyl.}}{\left(\mathrm{Sn(C^2H^5)^4}\right)} + \underset{\text{Hydrochloric acid.}}{4\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{Cl}\end{matrix}\right\}\right)} = \underset{\text{Tetrachloride of tin.}}{\left(\left.\begin{matrix}\mathrm{Sn}\\ \mathrm{Cl^4}\end{matrix}\right\}\right)} + \underset{\text{Hydride of ethyl.}}{4\left(\mathrm{C^2H^6}\right)}$$

Thus the ethyl contained in these compounds may be eliminated atom by atom, and replaced by chlorine or iodine. The iodine can also be replaced by ethyl, and the lower ethylated compounds raised again to the saturated ethylide. Frankland and Buckton have found that tetrastannethyl is formed when the iodide of distannethyl is made to react on zinc ethyl:



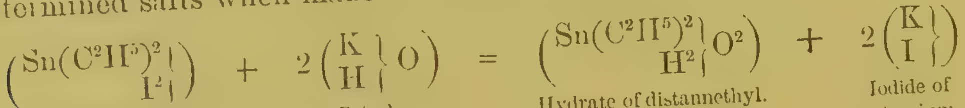
$$\left(\left.\begin{matrix}\mathrm{Sn(C^2H^5)^2}\\ \mathrm{I^2}\end{matrix}\right\}\right) + \left(\left.\begin{matrix}\mathrm{Zn''}\\ \mathrm{(C^2H^5)^2}\end{matrix}\right\}\right) = \left.\begin{matrix}\mathrm{Zn''}\\ \mathrm{I^2}\end{matrix}\right\} + \left(\mathrm{Sn(C^2H^5)^4}\right)$$

Iodidide of distannethyl. Zinc-ethyl. Iodide of zinc. Tetrastannethyl.

Cahours has also found that zinc-methyl reacts on the iodide of tristannethyl, giving a compound which represents tetrastannethyl a molecule of the ethyl of which is replaced by a molecule of methyl.

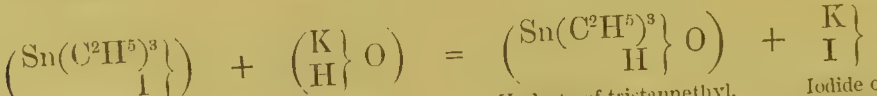
For a long time, tin having attributed to it an atomic weight the half of that we have adopted, tetrastannethyl was written $(\mathrm{Sn(C^2H^5)^2})$, and distannethyl $(\mathrm{Sn(C^2H^5)})$, while tristannethyl received the formula $(\mathrm{Sn^2(C^2H^5)^3})$. The vapour densities of the first two of these products necessitated the doubling of the formulæ; the well-marked reactions in which ethyl is successively replaced by chlorine or iodine, and the existence of a saturated double stannide of ethyl and methyl containing a single atom of the radicle methyl, demonstrate chemically that the molecular weights adopted for these bodies in accordance with their vapour densities, are the real ones. Consequently tin would always enter into these compounds by two atoms if the old atomic weight were attributed to it. This leads us to double this weight, because the atomic weight of a body is the smallest ponderal quantity which can enter into a molecule. The study of the stannides of ethyl therefore confirms the new atomic weight of tin.

The iodides of distannethyl and tristannethyl, treated with alkalies, give corresponding hydrates, which are basic and capable of giving well-determined salts when made to react with acids:



$$\left(\left.\begin{matrix}\mathrm{Sn(C^2H^5)^2}\\ \mathrm{I^2}\end{matrix}\right\}\right) + 2\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right) = \left(\left.\begin{matrix}\mathrm{Sn(C^2H^5)^2}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{O^2}\right) + 2\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{I}\end{matrix}\right\}\right)$$

Iodide of distannethyl. Potash. Hydrate of distannethyl. Iodide of potassium.



$$\left(\left.\begin{matrix}\mathrm{Sn(C^2H^5)^3}\\ \mathrm{I}\end{matrix}\right\}\right) + \left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right) = \left(\left.\begin{matrix}\mathrm{Sn(C^2H^5)^3}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right) + \left.\begin{matrix}\mathrm{K}\\ \mathrm{I}\end{matrix}\right\}$$

Iodide of tristannethyl. Potash. Hydrate of tristannethyl. Iodide of potassium.

On substituting iodide of methyl for iodide of ethyl in the above processes, methylic compounds are obtained which are analogous to the preceding in their formulæ and properties.

On account of the formulæ by which the stannides of ethyl and methyl were formerly represented, the compounds we call tetrastannethyl and tetrastannmethyl have hitherto been called distannethyl and distannmethyl; those we call tristannethyl and tristannmethyl were called sesquistannethyl and sesquistannmethyl; whilst distannethyl and distannmethyl were called stanethyl and stanmethyl.

**Plumb-ethyl and Plumbo-methyl.**—The ethylide and methylide of lead may be obtained by causing iodide of ethyl or iodide of methyl to react with an alloy of lead and sodium, but these compounds are more readily prepared by causing zinc-ethyl or zinc-methyl to react with chloride of lead.

The compounds formed in these reactions have the formulæ $(Pb(C^2H^5)^4)$ and $(Pb(CH^3)^4)$. The reaction which gives rise to them is the following:

$$\underset{\text{Chloride of lead.}}{2(PbCl^2)} + \underset{\text{Zinc-ethyl, or zinc-methyl.}}{\begin{matrix}2[Zn(C^2H^5)^2]\\ \text{or}\\ 2[Zn(CH^3)^2]\end{matrix}} = \underset{\text{Chloride of zinc.}}{2\left(\left.\begin{matrix}Zn\\Cl^2\end{matrix}\right\}\right)} + \underset{\text{Lead.}}{Pb} + \underset{\text{Plumb-ethyl, or plumbo-methyl.}}{\begin{matrix}(Pb(C^2H^5)^4)\\ \text{or}\\ (Pb(CH^3)^4)\end{matrix}}$$

Plumb-ethyl and plumb-methyl represent the limit of saturation of plumbic compounds, and therefore they do not act as radicles. But if these bodies be heated with hydrochloric acid or iodine, a molecule of ethyl or of methyl is eliminated in the state of hydride or of iodide, and bodies arise the composition of which is represented by the formulæ $(Pb(C^2H^5)^3I)$, $(Pb(C^2H^5)^3Cl)$, $(Pb(CH^3)^3I)$, and $(Pb(CH^3)^3Cl)$. The reactions by which these compounds are produced are expressed by the following equations:

$$\underset{\text{Plumb-ethyl.}}{(Pb(C^2H^3)^4)} + \underset{\text{Iodine.}}{\left.\begin{matrix}I\\I\end{matrix}\right\}} = \underset{\text{Iodide of ethyl.}}{\left(\left.\begin{matrix}C^2H^5\\I\end{matrix}\right\}\right)} + \underset{\text{Iodide of plumbo-triethyl.}}{(Pb(C^2H^5)^3I)}$$

$$\underset{\text{Plumbo-methyl.}}{(Pb(CH^3)^4)} + \underset{\text{Hydrochloric acid.}}{(HCl)} = \underset{\text{Hydride of methyl.}}{(CH^4)} + \underset{\text{Chloride of plumbo-trimethyl.}}{(Pb(CH^3)^3Cl)}$$

The existence of plumb-ethyl and of plumbo-methyl has already been used to demonstrate the tetratomicity of lead.

**Ethylide and Methylide of Mercury.** — With alcohol radicles mercury forms compounds of two orders; with ethyl or methyl we have:

Mercurous methyl $Hg''(CH^3)$; mercurous-ethyl $Hg''(C^2H^5)$.

Mercuric methyl $Hg''(CH^3)^2$; mercuric ethyl $Hg''(C^2H^5)^2$.

When the iodides of ethyl or of methyl are made to act on mercury, products are formed which are represented by the formulæ $(Hg(C^2H^5)I)$ and $(Hg(CH^3)I)$. These compounds are regarded as the iodides of special monatomic radicles, mercurous ethyl $Hg''(C^2H^5)$ and mercurous methyl $Hg''(CH^3)$. These radicles do not exist in a free state. It is very evident that, if they could be isolated, their molecules would be $\left(\left.\begin{matrix}Hg''(C^2H^5)\\Hg''(C^2H^5)\end{matrix}\right\}\right)$ and $\left(\left.\begin{matrix}Hg''(CH^3)\\Hg''(CH^3)\end{matrix}\right\}\right)$, as radicles of uneven atomicity cannot become free without combining with themselves.

Chlorine, bromine, cyanogen, and even the group HO may be substituted for iodine in the iodides of mercurous ethyl or mercurous methyl. In the last-mentioned case, hydrates are obtained which react with acids and give rise to salts.

If zinc-ethyl or zinc-methyl be made to react with the iodides of mercurous ethyl or mercurous methyl, either the mercuric ethyl, or the mercuric methyl, or the mercuric methylethyl are obtained:

$$\underset{\text{Iodide of mercurous ethyl.}}{2[Hg''(C^2H^5)I]} + \underset{\text{Zinc-ethyl.}}{(Zn''(C^2H^5)^2)} = \underset{\text{Iodide of zinc.}}{\left.\begin{matrix}Zn''\\ I^2\end{matrix}\right\}} + \underset{\text{Mercuric ethyl.}}{2[Hg''(C^2H^5)^2]}$$

$$\underset{\text{Iodide of mercurous-methyl.}}{2[Hg''(CH^3)I]} + \underset{\text{Zinc-methyl.}}{(Zn''(CH^3)^2)} = \underset{\text{Iodide of zinc.}}{\left.\begin{matrix}Zn''\\ I^2\end{matrix}\right\}} + \underset{\text{Mercuric methyl.}}{2[Hg''(CH^3)^2]}$$

$$\underset{\text{Iodide of mercurous-ethyl.}}{2[Hg''(C^2H^5)I]} + \underset{\text{Zinc-methyl.}}{(Zn''(CH^3)^2)} = \underset{\text{Iodide of zinc.}}{\left.\begin{matrix}Zn''\\ I^2\end{matrix}\right\}} + \underset{\text{Mercuric-methyl-ethyl.}}{2[Hg''(C^2H^5)(CH^3)]}$$

With amyl and allyl mercury forms corresponding compounds which possess analogous properties, and are represented by corresponding formulæ.

Messrs. Frankland and Duppa have recently succeeded in preparing mercuric ethyl, mercuric methyl, and mercuric amyl in a much more simple manner. They heat a mixture of sodium amalgam, iodide of methyl, ethyl, or amyl, and acetic ether. This latter merely acts by catalysis. The heat is continued to distillation, the product is washed first with an alkaline solution and then with water, dried, and again rectified. In the case of mercuric amyl, it must be distilled in a current of aqueous vapour or the body will decompose.

The compounds of mercury with an alcohol radicle have this property, that when heated with zinc, cadmium, or even aluminium, the mercury is displaced by these metals. They therefore furnish a very simple method of obtaining the organo-metallic compounds of zinc, cadmium or aluminium.

We have already pointed out what support the organo-metallic compounds of mercury give to the atomic weight used for this metal.

**Silicides of Ethyl and Methyl.**—Friedel and Crafts have obtained silicon-ethyl by heating for three hours at 160°, in an hermetically-sealed tube, a mixture of chloride of silicon and zinc-ethyl, containing two molecules of the second of these bodies for each molecule of the first.

When the tube is opened the gas is allowed to escape, and the product is distilled. What passes over below 130° contains silicon-ethyl mixed with unaltered chloride of silicon, and is placed aside to be afterwards heated with zinc-ethyl in a fresh operation.

That which remains in the retort after the temperature has reached 130°, is washed, first with water and then with an alkaline solution, in order to decompose the last traces of silicic chloride. It is then distilled with water, and the water which passes over with it is decanted.

The silicon-ethyl thus obtained still contains some traces of an oxygenized product, which is removed by agitating the liquid several times with concentrated sulphuric acid, in which silicon-ethyl is insoluble while the impurity is dissolved. Lastly, the product in sulphuric acid is washed with water, dried by chloride of calcium, and distilled. It is then perfectly pure.

Silicon-ethyl $\left(\mathrm{Si}^{\mathrm{iv}}\left\{\begin{matrix}\mathrm{C^2H^5}\\ \mathrm{C^2H^5}\\ \mathrm{C^2H^5}\\ \mathrm{C^2H^5}\end{matrix}\right.\right)$ boils at 153°; its vapour density has been found to be 5·13 (theoretically = 4·99). It is insoluble in water, alkaline solutions, concentrated sulphuric acid, nitric acid, and the acids in general. It is lighter than water, and burns with a very bright flame, emitting white vapours of silica.

Submitted to the action of chlorine, silicon-ethyl exchanges an atom of hydrogen for that metalloid, and gives a compound ($\mathrm{C^8SiH^{19}Cl}$) which represents chloride of nonyl ($\mathrm{C^9H^{19}Cl}$), in which an atom of silicon takes the place of an atom of carbon:

$$\underset{\text{Silicon-ethyl.}}{\left(\mathrm{Si(C^2H^5)^4}\right)} + \underset{\text{Chlorine.}}{\left.\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right\}} = \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}\mathrm{H}\\ \mathrm{Cl}\end{matrix}\right\}} + \underset{\text{Chloride of silico-nonyl.}}{\left(\mathrm{SiC^8H^{19}Cl}\right)}$$

On treating this chloride with acetate of potassium dissolved in alcohol, MM. Friedel and Crafts have succeeded in replacing the chlorine by oxacetyl, and have obtained an acetic ether, which, when saponified by means of an alcoholic solution of potash, has furnished silico-nonylic alcohol $\left(\left.\begin{matrix}\mathrm{SiC^8H^{19}}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)$.

$$\text{1st. }\underset{\text{Chloride of silico-nonyl.}}{\left(\left.\begin{matrix}\mathrm{SiC^8H^{19}}\\ \mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\text{Acetate of potassium.}}{\left(\left.\begin{matrix}\mathrm{C^2H^3O}\\ \mathrm{K}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\text{Chloride of potassium.}}{\left.\begin{matrix}\mathrm{K}\\ \mathrm{Cl}\end{matrix}\right\}} + \underset{\text{Acetate of silico-nonyl.}}{\left(\left.\begin{matrix}\mathrm{SiC^8H^{19}}\\ \mathrm{C^2H^3O}\end{matrix}\right\}\mathrm{O}\right)}$$

$$\text{2nd. }\underset{\text{Acetate of silico-nonyl.}}{\left(\left.\begin{matrix}\mathrm{SiC^8H^{19}}\\ \mathrm{C^2H^3O}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Hydrate of potassium.}}{\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\text{Acetate of potassium.}}{\left(\left.\begin{matrix}\mathrm{C^2H^3O}\\ \mathrm{K}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Silico-nonylic alcohol.}}{\left(\left.\begin{matrix}\mathrm{SiC^8H^{19}}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}$$

Silicon-methyl $\left(\mathrm{S}^{\mathrm{iv}}\left\{\begin{matrix}\mathrm{CH^3}\\ \mathrm{CH^3}\\ \mathrm{CH^3}\\ \mathrm{CH^3}\end{matrix}\right.\right)$ has been prepared by the same chemists, by an analogous method. They first heated zinc with iodide of methyl to 120° for several days, allowing the gases to escape occasionally, and then distilled. The product, which was a mixture of iodide of methyl and zinc-methyl, was placed in an hermetically-sealed tube with zinc and chloride of silicon. The object of the zinc is to transform the remainder of the iodide of methyl into zinc-methyl, to effect which the tube must first be heated to 120° for twelve hours; afterwards it must be heated to 200° for ten hours to produce the reaction of the zinc-methyl with the chloride of silicon. The contents of the tube are distilled, and the product condensed by a mixture of ice and salt, washed with an aqueous solution of potash to decompose the silicic chloride or the unattacked zinc-methyl. Finally, the silicon-methyl is submitted to distillation.

It is a liquid volatile at 30 – 31°, burning with a bright flame and emitting vapours of silica. Its vapour density determined by experiment is 3·058; theoretically, 3·045.

## OXYGENATED RADICLES.

Experience demonstrates that in hydrocarbon radicles O may be substituted for $H^2$ as often as there are non-saturated atoms of carbon united to $H^2$ in these radicles. Thus in ethyl $\left\{\begin{matrix}CH^3\\CH^2\end{matrix}\right.$ the substitution may take place once; in ethylene $\left\{\begin{matrix}CH^2\\CH^2\end{matrix}\right.$ twice; in glyceryl $\left\{\begin{matrix}CH^2\\CH\\CH^2\end{matrix}\right.$ twice. In the hypothetical radicle $\left(C\left\{\begin{matrix}CH^2\\CH^2\\CH^2\\CH^2\end{matrix}\right.\right)$ the substitution would be possible four times, and so on.

The oxygenated radicles thus produced give rise to a series of bodies parallel to that furnished by the hydrocarbon radicles whence they are derived. But, as they are electro-negative, they form acids when they combine with hydroxyl; hence they are called acid radicles.

Very few acid radicles are known in the isolated state, and it is not certain that the small number of bodies described as such, really have the constitution attributed to them.

The isolated acid radicles which have been described are: benzoyl $\left.\begin{matrix}C^7H^5O\\C^7H^5O\end{matrix}\right\}$, cuminyl $\left.\begin{matrix}C^{10}H^{11}O\\C^{10}H^{11}O\end{matrix}\right\}$, and butyryl $\left.\begin{matrix}C^4H^7O\\C^4H^7O\end{matrix}\right\}$.

These bodies may be obtained either by causing sodium amalgam to act on their chlorides:

$$\underset{\text{Chloride of butyryl.}}{2\left(\left.\begin{matrix}C^4H^7O\\Cl\end{matrix}\right\}\right)} + \underset{\text{Sodium.}}{\left.\begin{matrix}Na\\Na\end{matrix}\right\}} = \underset{\text{Chloride of sodium.}}{2\left(\left.\begin{matrix}Na\\Cl\end{matrix}\right\}\right)} + \underset{\text{Butyryl.}}{\left(\left.\begin{matrix}C^4H^7O\\C^4H^7O\end{matrix}\right\}\right)}$$

or by the action of their chlorides on a compound of the same radicle with an alkaline metal:

$$\underset{\text{Chloride of benzoyl.}}{\left(\left.\begin{matrix}C^7H^5O\\Cl\end{matrix}\right\}\right)} + \underset{\text{Benzoilide of potassium.}}{\left(\left.\begin{matrix}C^7H^5O\\K\end{matrix}\right\}\right)} = \underset{\text{Free benzoyl.}}{\left(\left.\begin{matrix}C^7H^5O\\C^7H^5O\end{matrix}\right\}\right)} + \underset{\text{Chloride of potassium.}}{\left.\begin{matrix}K\\Cl\end{matrix}\right\}}$$

The compounds of an alkaline metal with an acid radicle, of which we speak, are produced when an aldehyd is treated with a metal of this class:

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## MONATOMIC ACIDS.

$$2\left(\left.\begin{matrix}C^7H^5O\\ H\end{matrix}\right\}\right) + \left.\begin{matrix}K\\ K\end{matrix}\right\} = \left.\begin{matrix}H\\ H\end{matrix}\right\} + 2\left(\left.\begin{matrix}C^7H^5O\\ K\end{matrix}\right\}\right)$$

Benzoic aldehyd. Potassium. Hydrogen. Benzoilide of potassium.

Properties.—The properties of these bodies have as yet been very little studied; it is only known that, under the influence of caustic potash and heat, cuminyl gives cuminic acid and hydride of cuminyl:

$$\left(\left.\begin{matrix}C^{10}H^{11}O\\ C^{10}H^{11}O\end{matrix}\right\}\right) + \left(\left.\begin{matrix}K\\ H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}C^{10}H^{11}O\\ K\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}C^{10}H^{11}O\\ H\end{matrix}\right\}\right)$$

Cuminyl. Potash. Cuminate of potassium. Hydride of cuminyl.

No acid radicle having an atomicity greater than unity is known in the free state.

## ORGANIC ACIDS.

Organic acids are hydrates of oxygenated radicles. They may contain different quantities of typical hydrogen, hence they are naturally divided into mono, bi, tri, . . . *n* atomic.

Their atoms of typical hydrogen may, under the influence of powerful bases, be replaced by metals. This property constitutes the basicity of these acids. Their basicity is not always equal to their atomicity, for while it is evident that a monatomic acid must always be monobasic, biatomic acids may be either mono- or bi-basic, triatomic acids, mono, bi, or tri-basic, and so on.

## MONATOMIC ACIDS.

These acids are derived from alcohols of the same atomicity by the substitution of O for $H^2$, and they therefore all contain two atoms of oxygen. To each series of hydrocarbides there corresponds a series of alcohols, and to each of these also there corresponds a series of monatomic acids. Thus we have:

Hydrocarbides.

$C^nH^{2n+2}$ $C^nH^{2n}$ $C^nH^{2n-2}$ $C^nH^{2n-4}$ $C^nH^{2n-6}$ $C^nH^{2n-8}$ . . . etc.

Alcohols.

$C^nH^{2n+2}O$ $C^nH^{2n}O$ $C^nH^{2n-2}O$ $C^nH^{2n-4}O$ $C^nH^{2n-6}O$ $C^nH^{2n-8}O$. . etc.

Acids.

$C^nH^{2n}O^2$ $C^nH^{2n-2}O^2$ $C^nH^{2n-4}O^2$ $C^nH^{2n-6}O^2$ $C^nH^{2n-8}O^2$ $C^nH^{2n-10}O^2$ . etc.

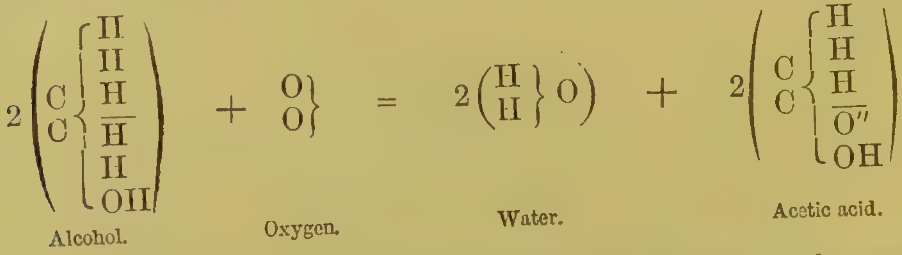
The most numerous and best known of these acids are those which belong to the series $C^nH^{2n}O^2$, $C^nH^{2n-2}O^2$, $C^nH^{2n-8}O^2$ and $C^{2n}H^{n-10}O^2$: only a few of the constituents of the other series are known.

The acids of the series $C^nH^{2n}O^2$ and $C^nH^{2n-8}O^2$ having a great number of characters in common, we will consider them together, and point out the particularities observed in each of these series.

The acids of the series $C^nH^{2n-2}O^2$ and $C^nH^{2n-10}O^2$ differ too much from the others in their constitution and properties to be included with them, and will therefore be studied separately.

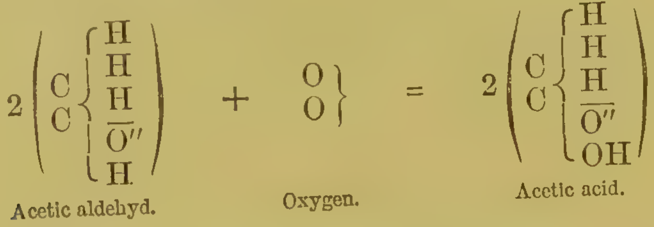
## ACIDS BELONGING TO THE SERIES $C^nH^{2n}O^2$ and $C^nH^{2n-8}O^2$.

PREPARATION.—*First Process.*—An alcohol is treated, in contact with air, by platinum black or by any other oxidant; water and the corresponding acid are produced:



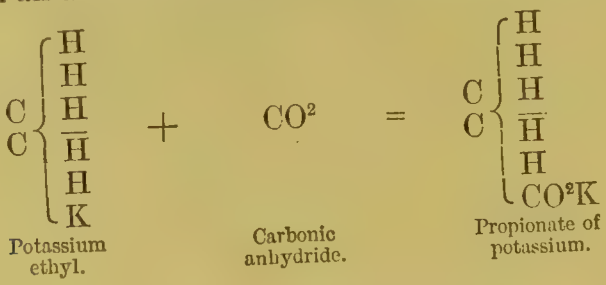
$$2\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H\\H\\H\\\overline{H}\\H\\OH\end{matrix}\right.\right)+\left.\begin{matrix}O\\O\end{matrix}\right\}=2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)+2\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H\\H\\H\\\overline{O''}\\OH\end{matrix}\right.\right)$$

*Second Process.*—Aldehyds are oxidized; they fix an atom of oxygen, and are transformed into acids:



$$2\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H\\H\\H\\\overline{O''}\\H\end{matrix}\right.\right)+\left.\begin{matrix}O\\O\end{matrix}\right\}=2\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H\\H\\H\\\overline{O''}\\OH\end{matrix}\right.\right)$$

*Third Process.*—Carbonic anhydride is made to act on a compound of potassium with an alcohol radicle:



$$\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H\\H\\H\\\overline{H}\\H\\K\end{matrix}\right.+CO^2=\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H\\H\\H\\\overline{H}\\H\\CO^2K\end{matrix}\right.$$

This process is not so general as the two preceding, on account of the difficulty of uniting potassium or sodium with the different alcohol radicles. Acetic and propionic acids are prepared by it.

*Fourth Process.*—In the aromatic series, Kékulé has succeeded in preparing benzoic acid and its homologues synthetically, by causing sodium and carbonic anhydride to act simultaneously on the monobrominated fundamental hydrocarbides of the lower series (benzine, toluene, etc.).

$$\underset{\text{Monobrominated benzine.}}{\left(C^6H^5Br\right)} + \underset{\text{Sodium.}}{\left.\begin{matrix}Na\\Na\end{matrix}\right\}} + \underset{\text{Carbonic anhydride.}}{\left(CO^2\right)}$$

$$= \underset{\text{Bromide of sodium.}}{\left(\left.\begin{matrix}Na\\Br\end{matrix}\right\}\right)} + \underbrace{\left[\left(\left.\begin{matrix}C^6H^5\\CO^2Na\end{matrix}\right\}\right) = \left(\left.\begin{matrix}C^7H^5O\\Na\end{matrix}\right\}O\right)\right]}_{\text{Benzoate of sodium.}}$$

This method, though differing in form from the preceding one, is really the same, slightly modified.

*Fifth Process.*—A solution of potash in alcohol is heated with the cyanide of a radicle of alcohol; ammonia is set free, and there is produced a salt of the acid which corresponds to the higher homologue of the alcohol, the hydrocyanic ether of which was employed:

$$\text{Ex.}\quad \underbrace{\left(\begin{matrix}CH^3\\CN\end{matrix}\right) = \left(C^2H^{3'''}N\right)}_{\text{Cyanide of methyl.}} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

$$= \underset{\text{Acetate of potassium.}}{\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right)} + \underset{\text{Ammonia.}}{\left(NH^3\right)}$$

It will be seen that the cyanide of methyl, derived from methylic alcohol ($CH^4O$), gives acetic acid, which is derived from ethylic alcohol ($C^2H^6O$), the next higher homologue of the methylic alcohol.

This process is general; but Cannizzaro states that in the aromatic series, that is to say, in the series in which the hydrocarbides have the formula $C^nH^{2n-6}$, the acids obtained by means of the cyanides do not constitute the true homologues of those derived from the same alcohol as the cyanide employed, but that they are simply isomers of these latter.

Thus benzoic alcohol ($C^7H^8O$) corresponds to benzoic acid ($C^7H^6O^2$); with the hydrocyanic ether of this alcohol an acid is obtained, the formula of which is ($C^8H^8O^2$); and this formula appears to be homologous with benzoic acid, but in reality it is only an isomer of the true homologue, which is known, and which possesses different properties.

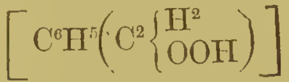
Kékulé thus explains this isomerism: as has been already said, benzine, according to this chemist, is formed of six atoms of carbon united to each other on one side by one, and on the other by two atomicities, so as to form an hexatomic group, which is saturated by hydrogen.

If methyl, ethyl, or amyl be substituted for one or more atoms of hydrogen of the benzine, homologues of this body are obtained. With the exception of toluene which contains a single methyl group, all the homologues of benzine can present cases of isomerism which should be reproduced in the acids and alcohols derived from these hydrocarbides. Thus two isomers (actually known) [$C^6H^5(C^2H^5)$] and [$C^6H^4(CH^3)^2$] may be supposed for xylene, and these should therefore give rise to two isomeric acids and to two isomeric alcohols.

Kékulé, admitting, as will be seen presently (*see* Phenols), that in the aromatic alcohols the hydroxyl substituted for H is found in one of the methyl and ethyl groups, the two alcohols which correspond to the two above hydrocarbides should therefore be

$$[C^6H^5(C^2H^4OH)] \quad \text{and} \quad [C^6H^4(CH^3)(CH^2OH)]$$

Let us now suppose that the second of these alcohols is oxidized. O would be substituted for $H^2$, and there would arise an acid $[C^6H^4(CH^3)(CO,OH)]$. If the other were oxidized, an acid would be obtained which would be isomeric with the preceding, and would correspond to the formula:



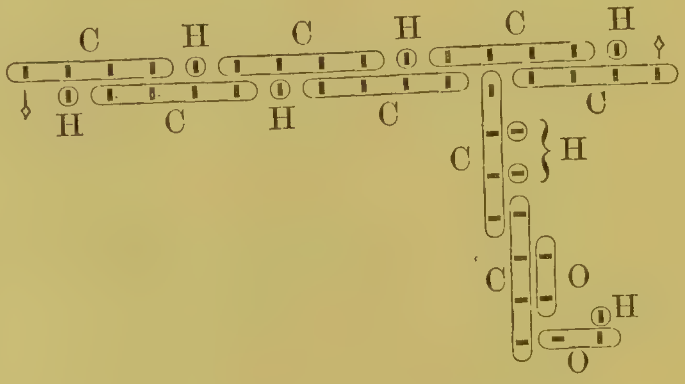
$$\left[C^6H^5\left(C^2\begin{cases}H^2\\OOH\end{cases}\right)\right]$$

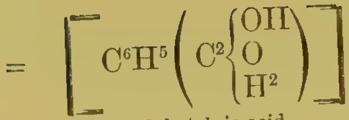
This acid would be the same as is obtained by the action of potash on the cyanide of benzyl. When the cyanide of benzyl is prepared by means of toluene $[C^6H^5(CH^3)]$, CN is substituted for H in the methyl group, the cyanide of benzyl is therefore $[C^6H^5(CH^2,CN)]$.

As the transformation of the alcoholic cyanides into acids consists in the substitution of the group $(O^2H)$ for nitrogen, the acid prepared from the cyanide of benzyl is

$$[C^6H^5(CH^2CO^2H)]$$

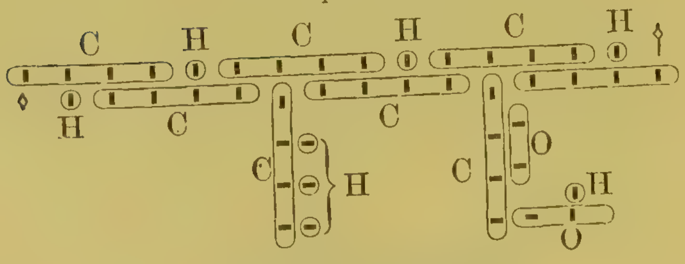
The following figures show this isomerism of the acids obtained from the cyanides of aromatic alcohols, with those prepared by other methods.





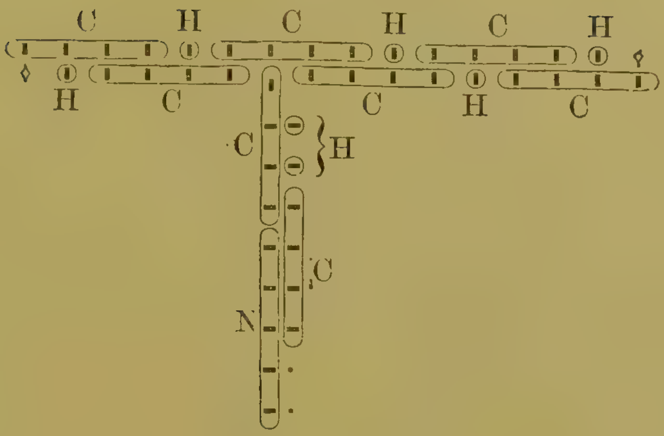
$$= \left[C^6H^5\left(C^2\begin{cases}OH\\O\\H^2\end{cases}\right)\right]$$

Alphatoluic acid.

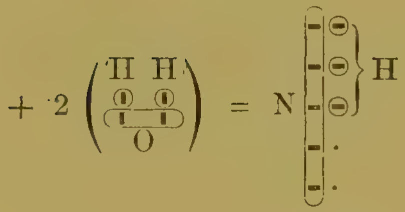


$$= [C^6H^4(CH^3)(CO^2H)]$$

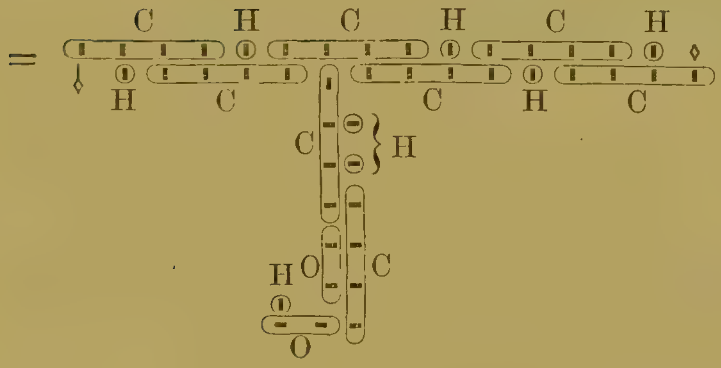
Toluic acid (Noad's.)



Cyanide of benzyl.



Water. Ammonia.



Alphatoluic acid.

This last figure clearly shows that the hydration of cyanide of benzyl ought to furnish alphatoluic acid and not Noad's toluic acid.

*Sixth Process.*—Monatomic acids may be prepared by treating the chloride of their radicle with water; hydrochloric acid is produced at the same time.

$$\underset{\text{Chloride of acetyl.}}{\left(\begin{matrix}C^2H^3O\\Cl\end{matrix}\right\}\Big)} + \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O} = \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}} + \underset{\text{Acetic acid.}}{\left(\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O\right)}$$

This process has become interesting since M. Harnitz-Harnitzky has obtained the chlorides of benzoyl, acetyl, and caproyl, synthetically, by causing the oxychloride of carbon to act on benzine in vapour, marsh gas, and hydride of amyl:

$$\underset{\text{Benzine.}}{\left(C^6H^6\right)} + \underset{\text{Oxychloride of carbon.}}{\left(C^{IV}\left\{\begin{matrix}Cl\\O''\\Cl\end{matrix}\right.\right)} = \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}} = \underset{\text{Chloride of benzoyl.}}{\left(C^{IV}\left\{\begin{matrix}C^6H^5\\O''\\Cl\end{matrix}\right.\right)}$$

$$\underset{\text{Marsh gas.}}{\left(CH^4\right)} + \underset{\text{Oxychloride of carbon.}}{\left(C^{IV}\left\{\begin{matrix}Cl\\O''\\Cl\end{matrix}\right.\right)} = \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}} + \underset{\text{Chloride of acetyl.}}{\left(C^{IV}\left\{\begin{matrix}CH^3\\O''\\Cl\end{matrix}\right.\right)}$$

$$\underset{\text{Hydride of amyl.}}{\left(C^5H^{12}\right)} + \underset{\text{Oxychloride of carbon.}}{\left(C^{IV}\left\{\begin{matrix}Cl\\O''\\Cl\end{matrix}\right.\right)} = \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}} + \underset{\text{Chloride of caproyl.}}{\left(C\left\{\begin{matrix}C^5H^{11}\\O''\\Cl\end{matrix}\right.\right)}$$

All the preceding processes are, or may become general. Those which follow are only successful in certain series.

*Seventh Process.*—Caustic potash is caused to act on bodies which are capable of combining directly with it under the influence of a more or less elevated temperature. Potassic salts are formed, from which the free acid is prepared.

Only two examples of this mode of forming acids are known: that of formic acid, which is procured by means of the oxide of carbon, and that of campholic acid, which is formed by means of camphor:

$$\underset{\text{Potash.}}{\left(KHO\right)} + \underset{\text{Oxide of carbon.}}{\left(CO\right)} = \underset{\text{Formiate of potassium.}}{\left(\left.\begin{matrix}CHO\\K\end{matrix}\right\}O\right)}$$

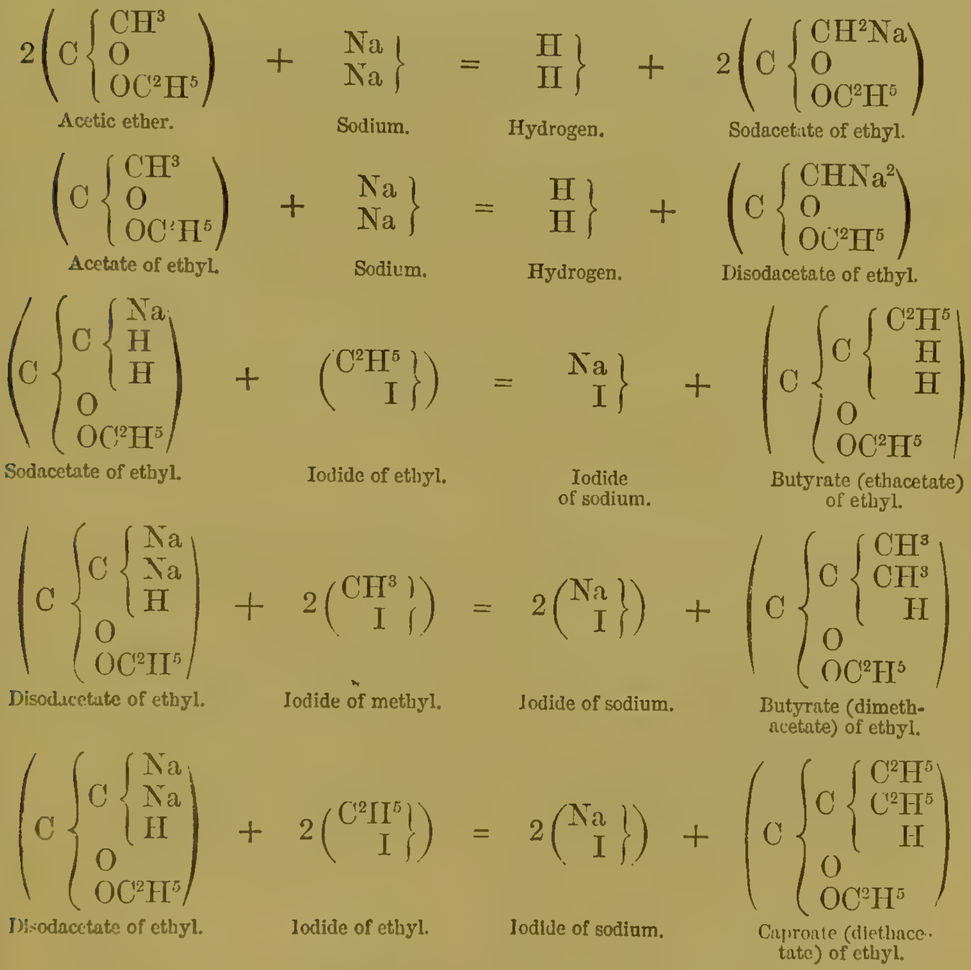
$$\underset{\text{Potash.}}{\left(KHO\right)} + \underset{\text{Camphor.}}{\left(C^{10}H^{16}O\right)} = \underset{\text{Potassic campholate.}}{\left(\left.\begin{matrix}C^{10}H^{17}O\\K\end{matrix}\right\}O\right)}$$

*Eighth Process.*—Certain acids are capable of fixing hydrogen and giving rise to acids more hydrogenized than themselves. It is thus that acids of the series $C^nH^{2n-2}O^2$ are transformed into fatty acids $C^nH^{2n}O^2$, and that Kolbe has succeeded in transforming benzoic acid ($C^7H^6O^2$) into hydro-benzoic acid ($C^8H^8O^2$).

It is possible, instead of fixing hydrogen on acids directly, first to fix bromine, for which hydrogen is afterwards substituted. By this method, cinnamic acid ($C^9H^8O^2$) has been transformed into a new acid corresponding to the formula ($C^9H^{10}O^2$). This new acid has also recently been produced by the direct action of nascent hydrogen on cinnamic acid.

*Ninth Process.*—Certain aromatic acids are obtained by the oxidation of certain hydrocarbides; it is remarked that in this case the hydrogen loses one of its lateral chains for which the group ($CO^2H$) is substituted. When it only contains one of these chains, it only furnishes a monatomic acid, but when it contains several, each of them may be successively exchanged for $(\mathrm{CO^2H})$, and bi, tri, etc., atomic acids are the results.

*Tenth Process.*—Frankland and Duppa have discovered a reaction which enables acetic acid to be transformed directly into its higher homologues. This is done by causing sodium to act on the acetate of ethyl. Sodium is substituted for one or two atoms of hydrogen in the radicle acetyl. Then, on causing the iodide of methyl or of ethyl to act on the mono- or bi-sodic product thus prepared, a sodic iodide and the ethylic ethers of the different homologues of acetic acid are obtained.



$$2\left(\mathrm{C}\begin{cases}\mathrm{CH^3}\\ \mathrm{O}\\ \mathrm{OC^2H^5}\end{cases}\right) + \left.\begin{matrix}\mathrm{Na}\\ \mathrm{Na}\end{matrix}\right\} = \left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\} + 2\left(\mathrm{C}\begin{cases}\mathrm{CH^2Na}\\ \mathrm{O}\\ \mathrm{OC^2H^5}\end{cases}\right)$$

Acetic ether. Sodium. Hydrogen. Sodacetate of ethyl.

$$\left(\mathrm{C}\begin{cases}\mathrm{CH^3}\\ \mathrm{O}\\ \mathrm{OC^2H^5}\end{cases}\right) + \left.\begin{matrix}\mathrm{Na}\\ \mathrm{Na}\end{matrix}\right\} = \left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\} + \left(\mathrm{C}\begin{cases}\mathrm{CHNa^2}\\ \mathrm{O}\\ \mathrm{OC^2H^5}\end{cases}\right)$$

Acetate of ethyl. Sodium. Hydrogen. Disodacetate of ethyl.

$$\left(\mathrm{C}\begin{cases}\mathrm{C}\begin{cases}\mathrm{Na}\\ \mathrm{H}\\ \mathrm{H}\end{cases}\\ \mathrm{O}\\ \mathrm{OC^2H^5}\end{cases}\right) + \left(\left.\begin{matrix}\mathrm{C^2H^5}\\ \mathrm{I}\end{matrix}\right\}\right) = \left.\begin{matrix}\mathrm{Na}\\ \mathrm{I}\end{matrix}\right\} + \left(\mathrm{C}\begin{cases}\mathrm{C}\begin{cases}\mathrm{C^2H^5}\\ \mathrm{H}\\ \mathrm{H}\end{cases}\\ \mathrm{O}\\ \mathrm{OC^2H^5}\end{cases}\right)$$

Sodacetate of ethyl. Iodide of ethyl. Iodide of sodium. Butyrate (ethacetate) of ethyl.

$$\left(\mathrm{C}\begin{cases}\mathrm{C}\begin{cases}\mathrm{Na}\\ \mathrm{Na}\\ \mathrm{H}\end{cases}\\ \mathrm{O}\\ \mathrm{OC^2H^5}\end{cases}\right) + 2\left(\left.\begin{matrix}\mathrm{CH^3}\\ \mathrm{I}\end{matrix}\right\}\right) = 2\left(\left.\begin{matrix}\mathrm{Na}\\ \mathrm{I}\end{matrix}\right\}\right) + \left(\mathrm{C}\begin{cases}\mathrm{C}\begin{cases}\mathrm{CH^3}\\ \mathrm{CH^3}\\ \mathrm{H}\end{cases}\\ \mathrm{O}\\ \mathrm{OC^2H^5}\end{cases}\right)$$

Disodacetate of ethyl. Iodide of methyl. Iodide of sodium. Butyrate (dimethacetate) of ethyl.

$$\left(\mathrm{C}\begin{cases}\mathrm{C}\begin{cases}\mathrm{Na}\\ \mathrm{Na}\\ \mathrm{H}\end{cases}\\ \mathrm{O}\\ \mathrm{OC^2H^5}\end{cases}\right) + 2\left(\left.\begin{matrix}\mathrm{C^2H^5}\\ \mathrm{I}\end{matrix}\right\}\right) = 2\left(\left.\begin{matrix}\mathrm{Na}\\ \mathrm{I}\end{matrix}\right\}\right) + \left(\mathrm{C}\begin{cases}\mathrm{C}\begin{cases}\mathrm{C^2H^5}\\ \mathrm{C^2H^5}\\ \mathrm{H}\end{cases}\\ \mathrm{O}\\ \mathrm{OC^2H^5}\end{cases}\right)$$

Disodacetate of ethyl. Iodide of ethyl. Iodide of sodium. Caproate (diethacetate) of ethyl.

In these reactions, acids of the same composition arise when disodacetic ether is treated by iodide of methyl, or the monosodacetic ether by iodide of ethyl. It is probable that these acids are isomers, and not identical, but this interesting question has not yet been decided.

Hitherto this tenth method has been limited to the preparation of the acids which can be derived from acetic acid. There is, however, reason to suppose that it will become general.

PROPERTIES.—1st. When one of these acids is heated to redness with an excess of a base, it tends to form the hydride of the alcohol one term lower in the homologous series. Thus from acetic acid $(\mathrm{C^2H^4O^2})$, hydride of methyl ($CH^4$) is obtained; from benzoic acid ($C^7H^6O^2$), benzine ($C^6H^6$), etc.

$$\underset{\text{Acetic acid.}}{(C^2H^4O^2)} = \underset{\text{Carbonic anhydride.}}{(CO^2)} + \underset{\text{Hydride of methyl.}}{(CH^4)}$$

This character is clearly observed in the aromatic series and in acetic acid. In the case of the other acids, secondary reactions are produced between the carbonic anhydride and the hydrocarbide (*see* Hydrocarbides), but the reaction remains essentially the same.

2nd. When an intimate mixture of a calcium salt of one of these acids and formiate of calcium is distilled, calcic carbonate is obtained and a compound which differs from the original acid by an atom of oxygen less, and which is called aldehyd.

$$\underset{\text{Acetate of calcium.}}{\left(\left.\begin{matrix}(C^2H^3O)^2\\ Ca''\end{matrix}\right\}O^2\right)} + \underset{\text{Formiate of calcium.}}{\left(\left.\begin{matrix}(CHO)^2\\ Ca''\end{matrix}\right\}O^2\right)} = 2\underset{\text{Carbonate of calcium.}}{\left(\left.\begin{matrix}CO''\\ Ca''\end{matrix}\right\}O^2\right)} + 2\underset{\text{Aldehyd.}}{\left(C^2H^4O\right)}$$

3rd. When a calcic or baric salt of one of these acids is distilled, a reaction analogous to the preceding takes place; carbonate of calcium or of barium is formed, and a body which represents a double molecule of the original acid, deprived of a molecule of carbonic anhydride. This new body is called acetone.

$$\underset{\text{Acetate of calcium.}}{\left(\left.\begin{matrix}(C^2H^3O)^2\\ Ca''\end{matrix}\right\}O^2\right)} = \underset{\text{Carbonate of calcium.}}{\left(\left.\begin{matrix}CO''\\ Ca''\end{matrix}\right\}O^2\right)} + \underset{\text{Acetone.}}{\left(C^3H^6O\right)}$$

4th. Chlorine and bromine may be substituted, atom for atom, for part of the hydrogen of these acids; but there always remains one atom of hydrogen for which these metalloids cannot be substituted. This substitutive action of chlorine and bromine sometimes occurs in the cold, but often it requires the action of heat; it occasionally takes place in diffused light, but sometimes requires the intervention of solar radiation.

These substitutions may be represented by the following equations:

$$\underset{\text{Acetic acid.}}{(C^2H^4O^2)} + \underset{\text{Bromine.}}{\left.\begin{matrix}Br\\ Br\end{matrix}\right\}} = \underset{\text{Monobromacetic acid.}}{(C^2H^3BrO^2)} + \underset{\text{Hydrobromic acid.}}{\left.\begin{matrix}H\\ Br\end{matrix}\right\}}$$

$$\underset{\text{Butyric acid.}}{\left(C^4H^8O^2\right)} + 2\underset{\text{Bromine.}}{\left(\left.\begin{matrix}Br\\ Br\end{matrix}\right\}\right)} = 2\underset{\text{Hydrobromic acid.}}{\left(\left.\begin{matrix}H\\ Br\end{matrix}\right\}\right)} + \underset{\text{Bibromobutyric acid.}}{\left(C^4H^6Br^2O^2\right)}$$

In the aromatic series, the brominated derivatives may be obtained by submitting the argentic salts of these acids to the action of bromine in vapour. It is difficult to account for this reaction. Bromine holds quite a different place in brominated acids to that held by silver in the argentic salt. The only plausible explanation of this is that the reaction takes place in two stages: in the first hydrobromic acid and an argentic salt of the brominated acid would be produced; in the second the hydrobromic acid would react on the argentic salt and give rise to bromide of silver, setting free the brominated organic acid:

$$\text{1st.}\ \underset{\text{Cuminate of silver.}}{\left(\left.\begin{matrix}C^{10}H^{11}O\\ Ag\end{matrix}\right\}O\right)} + \underset{\text{Bromine.}}{\left.\begin{matrix}Br\\ Br\end{matrix}\right\}} = \underset{\text{Hydrobromic acid.}}{\left.\begin{matrix}H\\ Br\end{matrix}\right\}} + \underset{\text{Bromocuminate of silver.}}{\left(\left.\begin{matrix}C^{10}H^{10}BrO\\ Ag\end{matrix}\right\}O\right)}$$

$$\text{2nd.}\ \underset{\text{Bromocuminate of silver.}}{\left(\left.\begin{matrix}C^{10}H^{10}BrO\\ Ag\end{matrix}\right\}O\right)} + \underset{\text{Hydrobromic acid.}}{\left.\begin{matrix}H\\ Br\end{matrix}\right\}} = \underset{\text{Bromide of silver.}}{\left.\begin{matrix}Ag\\ Br\end{matrix}\right\}} + \underset{\text{Bromocuminic acid.}}{\left(\left.\begin{matrix}C^{10}H^{10}BrO\\ H\end{matrix}\right\}O\right)}$$

Iodine may also be substituted for the hydrogen of monatomic acids, by heating the corresponding brominated compounds with iodide of potassium:

$$\underset{\text{Bromacetic ether.}}{\left(\left.\begin{matrix}C^{2}H^{2}BrO\\ C^{2}H^{5}\end{matrix}\right\}O\right)} + \underset{\text{Iodide of potassium.}}{\left.\begin{matrix}K\\ I\end{matrix}\right\}} = \underset{\text{Iodacetic ether.}}{\left(\left.\begin{matrix}C^{2}H^{2}IO\\ C^{2}H^{5}\end{matrix}\right\}O\right)} + \underset{\text{Bromide of potassium.}}{\left.\begin{matrix}K\\ Br\end{matrix}\right\}}$$

But Kékulé has shown that such a substitution cannot take place directly. Hydriodic acid, in presence of iodized compounds, gives free iodine and re-forms the body whence the iodized compound was derived. Thus, as iodine could not give rise to a product of substitution without at the same time causing the production of hydriodic acid, a second reaction, the inverse of the first, would take place, and the bodies would return to their original state.

5th. When chlorinated or brominated acids are boiled with water and oxide of silver, the chlorine or bromine is separated in combination with silver, and each atom of these metalloids is replaced by the group HO. The new acids which are formed differ from the original acids by a number of atoms of oxygen equal to that of the atoms of chlorine or bromine these contained:

$$\text{Ex.}\ \underset{\text{Bromacetic acid.}}{2(C^{2}H^{3}BrO^{2})} + \underset{\text{Oxide of silver.}}{(Ag^{2}O)} + \underset{\text{Water.}}{(H^{2}O)} = \underset{\text{Bromide of silver.}}{2(AgBr)} + \underset{\text{Glycolic acid.}}{2(C^{2}H^{4}O^{3})}$$

$$\underset{\text{Bibromo-butyric acid.}}{(C^{4}H^{6}Br^{2}O^{2})} + \underset{\text{Oxide of silver.}}{(Ag^{2}O)} + \underset{\text{Water.}}{(H^{2}O)} = \underset{\text{Bromide of silver.}}{2(AgBr)} + \underset{\text{Binoxybutyric acid.}}{(C^{4}H^{8}O^{4})}$$

It will be seen that glycolic acid ($C^{2}H^{4}O^{3}$) differs from acetic acid ($C^{2}H^{4}O^{2}$) by an additional atom of oxygen, and that binoxybutyric acid ($C^{4}H^{8}O^{4}$) differs from butyric acid ($C^{4}H^{8}O^{2}$) by $+ O^{2}$. Trichloracetic and bichloracetic acids are not sufficiently stable to undergo these reactions, their molecule being entirely destroyed. In the aromatic series, the brominated derivatives of monatomic acids, at present known, do not exchange Br for OH under the influence of moist oxide of silver.

This substitution can only be effected by the action of fused potash, under the influence of which bromobenzoic acid is converted into salicylic acid.

6th. Monochlorinated or monobrominated acids, when submitted to the action of an alcoholic solution of ammonia, give rise to chloride or bromide of ammonium. There is formed at the same time a monamide of the acid, which contains an atom more of oxygen than the original acid of the chlorinated or brominated derivative.

Thus monochloracetic acid gives a glycolic monamide known as glycocoll; the bromobutyric acid, an oxybutyric monamide, etc.:

$$\underset{\text{Chloracetic acid.}}{(C^2H^3ClO^2)} + \underset{\text{Ammonia.}}{2(NH^3)} = \underset{\text{Chloride of ammonium.}}{(NH^4Cl)} + \underset{\text{Glycocoll.}}{(C^2H^5NO^2)}$$

7th. Alcohols do not react in the cold on the monatomic acids of these series, but if heated with these bodies, water is eliminated and a compound ether is formed. It has been seen when speaking of the alcohols, that, whatever may be the respective quantities of acid and alcohol employed, there always remains a part of each of these bodies in the free state.

8th. The chlorides, bromides, oxychlorides, and oxybromides of phosphorus act on the acids of this group and on their salts. The radicle of the acid passes to the state of chloride or bromide. If the terchloride or terbromide be used, the phosphorus is converted into phosphorous acid; if, on the contrary, the pentachloride, pentabromide, oxychloride, or oxybromide be employed, the phosphorus passes to the state of phosphoric acid. With the perchloride or perbromide, oxychloride or oxybromide is first produced, and afterwards decomposed:

$$\underset{\text{Benzoic acid.}}{(C^7H^6O^2)} + \underset{\text{Perchloride of phosphorus.}}{(PCl^5)} = \underset{\text{Oxychloride of phosphorus.}}{(PCl^3O)} + \underset{\text{Chloride of benzoyl.}}{\left(\left.\begin{matrix}C^7H^5O\\Cl\end{matrix}\right\}\right)} + \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}}$$

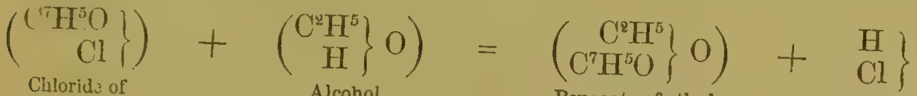
$$\underset{\text{Benzoic acid.}}{3(C^7H^6O^2)} + \underset{\text{Oxychloride of phosphorus.}}{(PCl^3O)} = \underset{\text{Phosphoric acid.}}{(PH^3O^4)} + \underset{\text{Chloride of benzoyl.}}{3\left(\left.\begin{matrix}C^7H^5O\\Cl\end{matrix}\right\}\right)}$$

$$\underset{\text{Acetic acid.}}{3(C^2H^4O^2)} + \underset{\text{Terchloride of phosphorus.}}{(PCl^3)} = \underset{\text{Phosphorous acid.}}{(PH^3O^3)} + \underset{\text{Chloride of acetyl.}}{3\left(\left.\begin{matrix}C^2H^3O\\Cl\end{matrix}\right\}\right)}$$

9th. These chlorides of acid radicles when placed in contact with water are decomposed and produce hydrobromic acid and the oxygenized acid the radicle of which they contain:

$$\underset{\text{Chloride of valeryl.}}{\left(\left.\begin{matrix}C^5H^9O\\Cl\end{matrix}\right\}\right)} + \underset{\text{Water.}}{H^2O} = \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}} + \underset{\text{Valeric acid.}}{\left(\left.\begin{matrix}C^5H^9O\\H\end{matrix}\right\}O\right)}$$

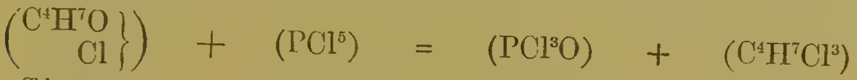
10th. With alcohols these acid chlorides form hydrochloric acid and a compound ether:



$$\left(\left.\begin{matrix}C^7H^5O\\ Cl\end{matrix}\right\}\right) + \left(\left.\begin{matrix}C^2H^5\\ H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}C^2H^5\\ C^7H^5O\end{matrix}\right\}O\right) + \left.\begin{matrix}H\\ Cl\end{matrix}\right\}$$

Chloride of benzoyl. Alcohol. Benzoate of ethyl. Hydrochloric acid.

11th. When heated with perchloride of phosphorus for several days to 200° in hermetically-sealed tubes, these chlorides undergo double decomposition: oxychloride of phosphorus is formed, and a compound which contains three atoms of chlorine, and which represents the terchlorinated derivative of the fundamental hydrocarbide of the series:

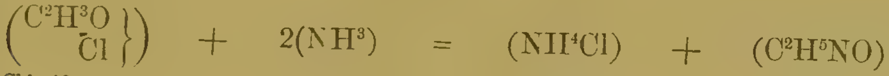


$$\left(\left.\begin{matrix}C^4H^7O\\ Cl\end{matrix}\right\}\right) + (PCl^5) = (PCl^3O) + (C^4H^7Cl^3)$$

Chloride of butyryl. Perchloride of phosphorus. Oxychloride of phosphorus.

The body $(C^4H^7Cl^3)$ is isomeric, and perhaps identical with the terchlorinated derivative of the fundamental hydrocarbide of the butyric series $(C^4H^{10})$.

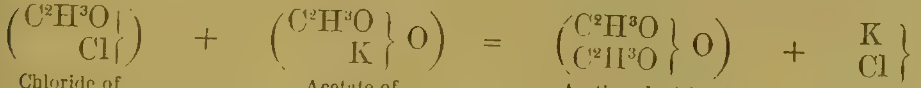
12th. These chlorides react energetically with ammoniacal gas, chloride of ammonium is produced, and the amide corresponding to the acid the radicle of which was contained in the chloride employed:



$$\left(\left.\begin{matrix}C^2H^3O\\ Cl\end{matrix}\right\}\right) + 2(NH^3) = (NH^4Cl) + (C^2H^5NO)$$

Chloride of acetyl. Ammonia. Chloride of ammonium. Acetamide.

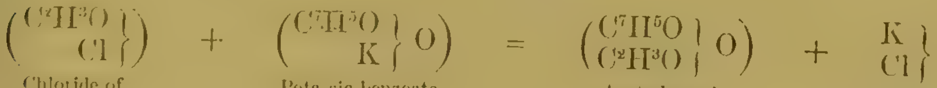
13th. These acid chlorides when distilled with a potassic salt of the acid the radicle of which they contain, give a metallic chloride and an anhydride of this acid:



$$\left(\left.\begin{matrix}C^2H^3O\\ Cl\end{matrix}\right\}\right) + \left(\left.\begin{matrix}C^2H^3O\\ K\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}C^2H^3O\\ C^2H^3O\end{matrix}\right\}O\right) + \left.\begin{matrix}K\\ Cl\end{matrix}\right\}$$

Chloride of acetyl. Acetate of potassium. Acetic anhydride. Chloride of potassium.

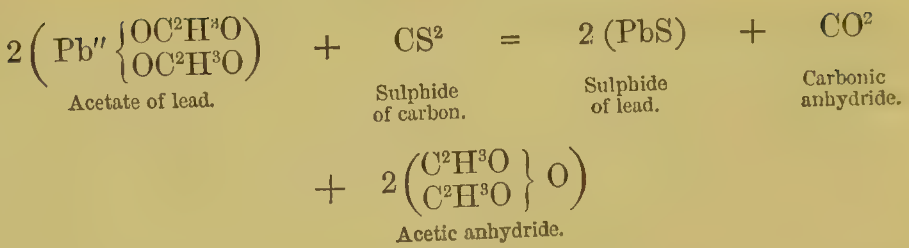
When distilled with a potassic salt of a different acid from the one whose radicle they contain, they form a mixed anhydride which contains the radicles of the two different acids:



$$\left(\left.\begin{matrix}C^2H^3O\\ Cl\end{matrix}\right\}\right) + \left(\left.\begin{matrix}C^7H^5O\\ K\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}C^7H^5O\\ C^2H^3O\end{matrix}\right\}O\right) + \left.\begin{matrix}K\\ Cl\end{matrix}\right\}$$

Chloride of acetyl. Potassic benzoate. Aceto-benzoic anhydride. Chloride of potassium.

These anhydrides may also be prepared by heating for several days to 165°, in hermetically-sealed tubes, a mixture of sulphide of carbon and a well-dried plumbic salt of the acid whose anhydride is desired:

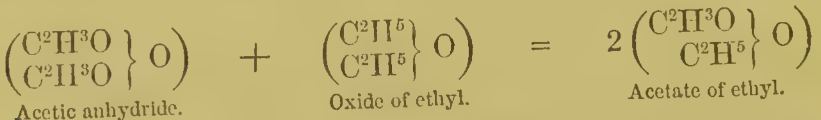


$$2\left(Pb''\left\{\begin{matrix}OC^2H^3O\\OC^2H^3O\end{matrix}\right.\right) + CS^2 = 2\,(PbS) + CO^2 + 2\left(\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O\right)$$

Acetate of lead. Sulphide of carbon. Sulphide of lead. Carbonic anhydride. Acetic anhydride.

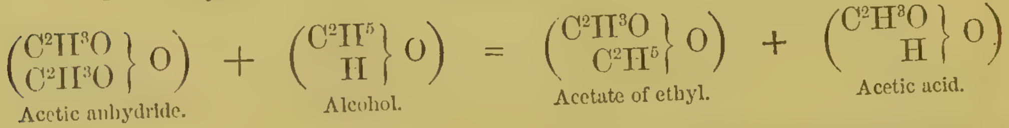
In this process it is necessary to open the tube daily, in order to let the carbonic anhydride escape and prevent explosion.

14th. Mixed with the ethers proper, acid anhydrides are transformed entirely into compound ethers. Mixed with alcohols, they give a mixture of compound ether and the normal acid:



$$\left(\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}O\right) = 2\left(\left.\begin{matrix}C^2H^3O\\C^2H^5\end{matrix}\right\}O\right)$$

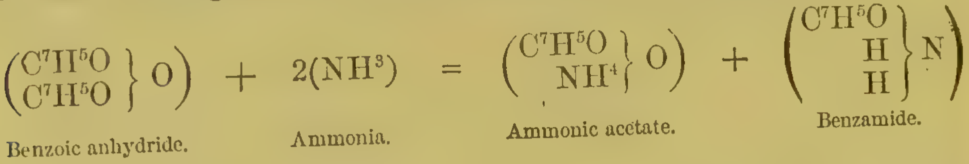
Acetic anhydride. Oxide of ethyl. Acetate of ethyl.



$$\left(\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}C^2H^3O\\C^2H^5\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O\right)$$

Acetic anhydride. Alcohol. Acetate of ethyl. Acetic acid.

15th. Submitted to the action of ammoniacal gas, the anhydrides of monobasic acids give a mixture of amide and ammoniacal salt:

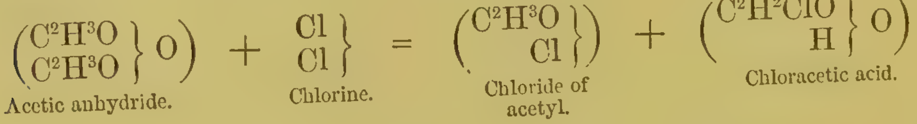


$$\left(\left.\begin{matrix}C^7H^5O\\C^7H^5O\end{matrix}\right\}O\right) + 2(NH^3) = \left(\left.\begin{matrix}C^7H^5O\\NH^4\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}C^7H^5O\\H\\H\end{matrix}\right\}N\right)$$

Benzoic anhydride. Ammonia. Ammonic acetate. Benzamide.

When a mixed anhydride is employed, one of the two radicles passes entirely to the state of amide, and the other to that of ammoniacal salt.

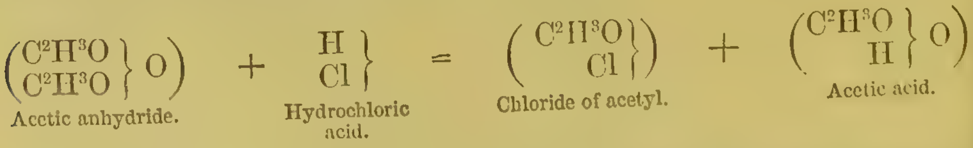
16th. Under the influence of chlorine, the anhydrides of monobasic acids split up; one of the two radicles passes to the state of chloride, and the residue formed by the other radicle and the atom of typical oxygen unites with a second atom of chlorine, and gives the monochlorinated derivative of the normal acid:



$$\left(\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O\right) + \left.\begin{matrix}Cl\\Cl\end{matrix}\right\} = \left(\left.\begin{matrix}C^2H^3O\\Cl\end{matrix}\right\}\right) + \left(\left.\begin{matrix}C^2H^2ClO\\H\end{matrix}\right\}O\right)$$

Acetic anhydride. Chlorine. Chloride of acetyl. Chloracetic acid.

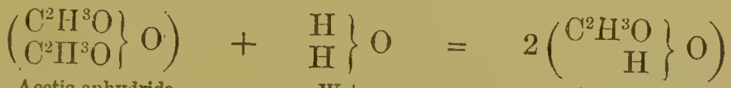
When hydrochloric acid is substituted for the chlorine, the reaction is of the same nature, only instead of a monochlorinated derivative of the normal acid, the acid itself is produced:



$$\left(\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O\right) + \left.\begin{matrix}H\\Cl\end{matrix}\right\} = \left(\left.\begin{matrix}C^2H^3O\\Cl\end{matrix}\right\}\right) + \left(\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O\right)$$

Acetic anhydride. Hydrochloric acid. Chloride of acetyl. Acetic acid.

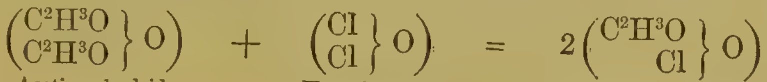
17th. With water, these anhydrides undergo double decomposition and furnish two molecules of hydrated acid for each molecule of anhydride :



$$\left(\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O\right) + \left.\begin{matrix}H\\H\end{matrix}\right\}O = 2\left(\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O\right)$$

Acetic anhydride. Water. Acetic acid.

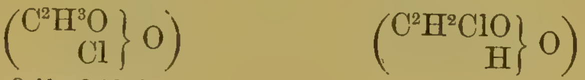
18th. When acted upon by hypochlorous anhydride, these anhydrides give a mixed oxide of chlorine and their acid radicle :



$$\left(\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}O\right) = 2\left(\left.\begin{matrix}C^2H^3O\\Cl\end{matrix}\right\}O\right)$$

Acetic anhydride. Hypochlorous anhydride. Oxide of chlorine and acetyl (acetate of chlorine).

These bodies are isomeric with the monochlorinated acids to which the anhydrides whence they are derived correspond :



$$\left(\left.\begin{matrix}C^2H^3O\\Cl\end{matrix}\right\}O\right) \qquad \left(\left.\begin{matrix}C^2H^2ClO\\H\end{matrix}\right\}O\right)$$

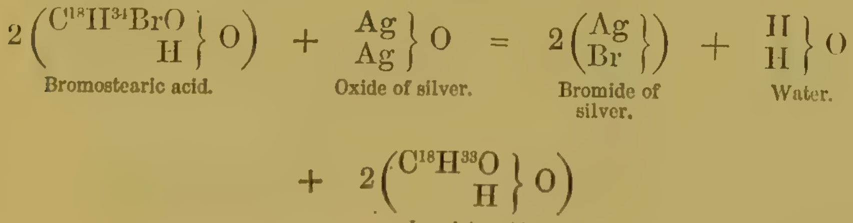
Oxide of chlorine and of acetyl. Monochloracetic acid.

19th. The monobasic acids of the series $C^nH^{2n}O^2$ (fatty acids) are capable of forming acid salts resulting from the juxtaposition of a molecule of acid and a molecule of a neutral salt. These salts cannot be considered as true atomic combinations. They are neutral salts in which a certain quantity of acid acts the part of water of crystallization.

## ACIDS BELONGING TO THE SERIES $C^nH^{2n-2}O^2$.

Preparation.—The natural acids of this series have each been prepared by a special process; oleic acid ($C^{18}H^{34}O^2$) has been extracted from oil by saponification ; pyroterebic acid ($C^6H^{10}O^2$) has been obtained by heating terebic acid; angelic acid ($C^5H^8O^2$) is found ready formed in the angelica root; crotonic acid ($C^4H^6O^2$) is extracted by saponification from the oil of *croton tiglium*, and acrylic acid is produced by oxidizing acrylic aldehyd ($C^3H^4O$) by oxide of silver. This aldehyd is formed by the action of bodies having great affinity for water on glycerine.

An acid isomeric with oleic acid has been obtained by submitting bromo-stearic acid to the action of oxide of silver :

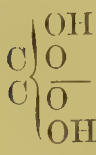


$$2\left(\left.\begin{matrix}C^{18}H^{34}BrO\\H\end{matrix}\right\}O\right) + \left.\begin{matrix}Ag\\Ag\end{matrix}\right\}O = 2\left(\left.\begin{matrix}Ag\\Br\end{matrix}\right\}\right) + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$
$$+\ 2\left(\left.\begin{matrix}C^{18}H^{33}O\\H\end{matrix}\right\}O\right)$$

Bromostearic acid. Oxide of silver. Bromide of silver. Water. Iso-oleic acid.

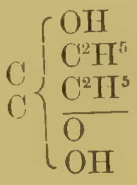
These processes are not general. But recently, Frankland has discovered a method of preparing acids of the series $C^nH^{2n-2}O^2$ synthetically. It is true that by this method he obtains, not the acids already known, but isomers of these. However, this synthesis has thrown such light on the constitution of all these acids, that Frankland hopes also to accomplish the synthesis of the natural acids.

As will be seen in biatomic and monobasic acids, Frankland has obtained acids resulting from the substitution either of two atoms of methyl or of two atoms of ethyl, or of an atom of methyl and one of ethyl, for the oxygen of oxalic acid:



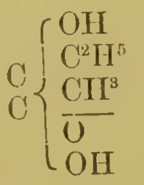
$$\begin{matrix}\mathrm{C}\\\mathrm{C}\end{matrix}\left|\begin{array}{l}\mathrm{OH}\\\mathrm{O}\\\hline\mathrm{O}\\\mathrm{OH}\end{array}\right.$$

Oxalic acid.



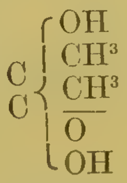
$$\begin{matrix}\mathrm{C}\\\mathrm{C}\end{matrix}\left\{\begin{array}{l}\mathrm{OH}\\\mathrm{C^2H^5}\\\mathrm{C^2H^5}\\\hline\mathrm{O}\\\mathrm{OH}\end{array}\right.$$

Biethoxalic acid.



$$\begin{matrix}\mathrm{C}\\\mathrm{C}\end{matrix}\left\{\begin{array}{l}\mathrm{OH}\\\mathrm{C^2H^5}\\\mathrm{CH^3}\\\hline\mathrm{O}\\\mathrm{OH}\end{array}\right.$$

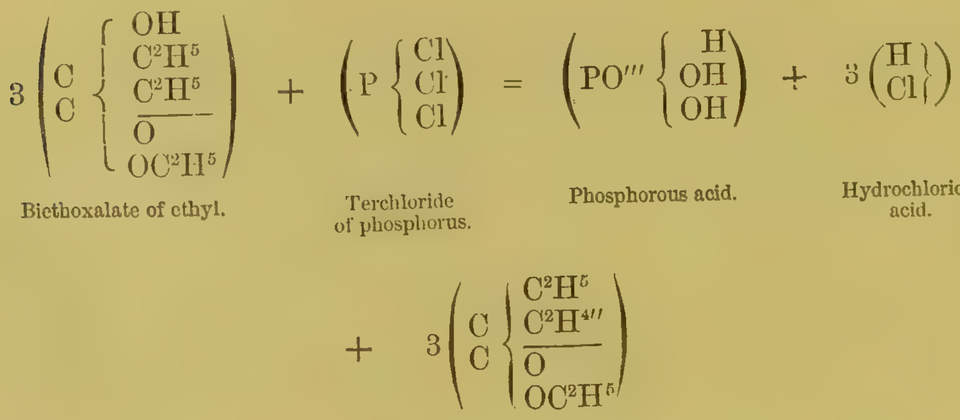
Etho-methoxalic acid.



$$\begin{matrix}\mathrm{C}\\\mathrm{C}\end{matrix}\left\{\begin{array}{l}\mathrm{OH}\\\mathrm{CH^3}\\\mathrm{CH^3}\\\hline\mathrm{O}\\\mathrm{OH}\end{array}\right.$$

Bimethoxalic acid.

The ethers of these acids, acted upon either by phosphoric anhydride or by the terchloride of phosphorus, each lose $H^2O$. This water is formed at the expense of an atom of hydroxyl, and an atom of hydrogen taken from one of the alcohol radicles. This latter radicle also becomes biatomic, and saturates that atomicity of the carbon set free by the elimination of OH.

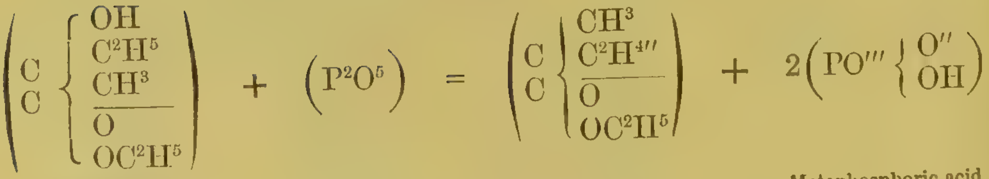


$$3\left(\begin{matrix}\mathrm{C}\\\mathrm{C}\end{matrix}\left\{\begin{array}{l}\mathrm{OH}\\\mathrm{C^2H^5}\\\mathrm{C^2H^5}\\\hline\mathrm{O}\\\mathrm{OC^2H^5}\end{array}\right.\right)+\left(\mathrm{P}\left\{\begin{array}{l}\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}\end{array}\right.\right)=\left(\mathrm{PO'''}\left\{\begin{array}{l}\mathrm{H}\\\mathrm{OH}\\\mathrm{OH}\end{array}\right.\right)+3\left(\begin{array}{l}\mathrm{H}\\\mathrm{Cl}\end{array}\right\}\right)$$

Biethoxalate of ethyl. Terchloride of phosphorus. Phosphorous acid. Hydrochloric acid.

$$+\;3\left(\begin{matrix}\mathrm{C}\\\mathrm{C}\end{matrix}\left\{\begin{array}{l}\mathrm{C^2H^5}\\\mathrm{C^2H^{4''}}\\\hline\mathrm{O}\\\mathrm{OC^2H^5}\end{array}\right.\right)$$

Ethylcrotonate of ethyl.



$$\left(\begin{matrix}\mathrm{C}\\\mathrm{C}\end{matrix}\left\{\begin{array}{l}\mathrm{OH}\\\mathrm{C^2H^5}\\\mathrm{CH^3}\\\hline\mathrm{O}\\\mathrm{OC^2H^5}\end{array}\right.\right)+\left(\mathrm{P^2O^5}\right)=\left(\begin{matrix}\mathrm{C}\\\mathrm{C}\end{matrix}\left\{\begin{array}{l}\mathrm{CH^3}\\\mathrm{C^2H^{4''}}\\\hline\mathrm{O}\\\mathrm{OC^2H^5}\end{array}\right.\right)+2\left(\mathrm{PO'''}\left\{\begin{array}{l}\mathrm{O''}\\\mathrm{OH}\end{array}\right.\right)$$

Ethomethoxalate of ethyl. Phosphoric anhydride. Methylcrotonate of ethyl. Metaphosphoric acid.

$$3\left[\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}OH\\CH^3\\CH^3\\ \hline O\\OC^2H^5\end{matrix}\right.\right] + \left(P\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right.\right) = \left(PO'''\left\{\begin{matrix}H\\OH\\OH\end{matrix}\right.\right) + 3\left[\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}CH^3\\CH^{2''}\\ \hline O\\OC^2H^5\end{matrix}\right.\right]$$

Bimethoxalate of ethyl. Terchloride of phosphorus. Phosphorous acid. Methacrylate of ethyl.

$$+ \quad 3\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)$$

Hydrochloric acid.

Lastly, we have to mention the preparation of an acid of the formula ($C^4H^6O^2$), isomeric or identical with the preceding, which Claus has obtained by boiling cyanide of allyl with caustic potash:

$$\left(\left.\begin{matrix}C^3H^5\\CN\end{matrix}\right\}\right) + \left.\begin{matrix}K\\H\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}O = N\left\{\begin{matrix}H\\H\\H\end{matrix}\right. + \left(C^4H^5KO^2\right)$$

Cyanide of allyl. Potash. Water. Ammonia. Potassic crotonate.

PROPERTIES.—1st. Probably both the natural and artificial acids of this series would directly fix two atoms of bromine, if they were acted upon by this metalloid, and would give a bibrominated acid of the series $C^nH^{2n}O^2$:

$$\left(C^4H^6O^2\right) + \left.\begin{matrix}Br\\Br\end{matrix}\right\} = \left(C^4H^6Br^2O^2\right)$$

Crotonic acid. Bromine. Bibromobutyric acid.

2nd. The natural acids submitted to the action of nascent hydrogen combine with this body, and are transformed into acids of the series $C^nH^{2n}O^2$:

$$\left(C^4H^6O^2\right) + \left.\begin{matrix}H\\H\end{matrix}\right\} = \left(C^4H^8O^2\right)$$

Crotonic acid. Hydrogen. Butyric acid.

It is probable that the artificial acids would react in the same manner.

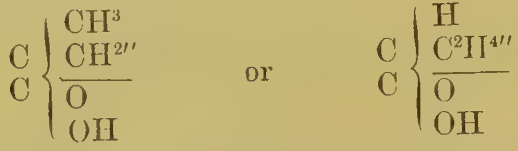
3rd. Submitted to the influence of potash in a state of fusion, the acids of this series, whether natural or artificial, disengage hydrogen, and are transformed into potassic salts of two acids of the series $C^nH^{2n}O^2$:

$$\left(C^{18}H^{34}O^2\right) + 2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right) = \left(C^{16}H^{31}KO^2\right) + \left(C^2H^3KO^2\right) + \left.\begin{matrix}H\\H\end{matrix}\right\}$$

Oleic acid. Potash. Palmitate of potassium. Acetate of potassium. Hydrogen.

*Constitution.*—In order to determine the constitution of these acids it is important first to understand how their division under the influence of potash takes place.

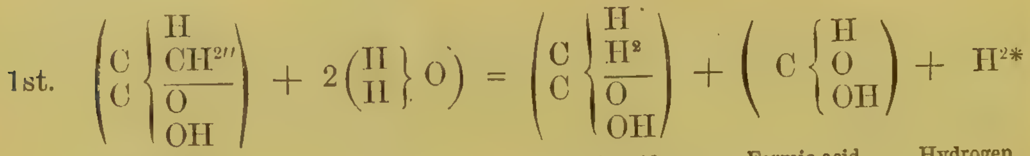
Thus, when acrylic acid is considered, it will be seen that this acid, the last in the series, can have no isomer, as no radicle can be substituted in a body having the formula $\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H\\CH^{2\prime\prime}\\\hline O\\OH\end{array}\right.\right)$ without altering its composition. This would not be the case with its homologues. The acid ($C^4H^6O^2$) may be written either



$$\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}CH^3\\CH^{2\prime\prime}\\\hline O\\OH\end{array}\right. \quad \text{or} \quad \begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H\\C^2H^{4\prime\prime}\\\hline O\\OH\end{array}\right.$$

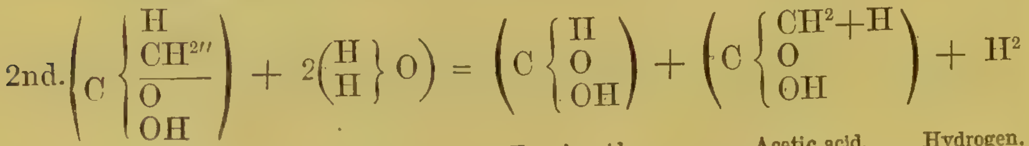
We know that with fused potassic hydrate, acrylic acid is converted into potassic formiate and acetate, hydrogen being disengaged. This reaction may be viewed in two different ways:

Either the group $CH^2$ contained in acrylic acid is replaced by $H^2$, which furnishes the acetic acid, while by absorbing $O^2$ it is itself transformed into formic acid. Such a reaction is expressed by the following equation:



$$\text{1st.}\ \underset{\text{Acrylic acid.}}{\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H\\CH^{2\prime\prime}\\\hline O\\OH\end{array}\right.\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Acetic acid.}}{\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H\\H^2\\\hline O\\OH\end{array}\right.\right)} + \underset{\text{Formic acid.}}{\left(C\left\{\begin{array}{l}H\\O\\OH\end{array}\right.\right)} + \underset{\text{Hydrogen.}}{H^2}*$$

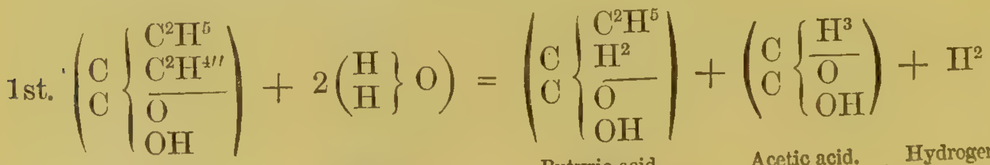
Or the group $C^2$ of acrylic acid is divided in this reaction, which would then be expressed by the following equation:



$$\text{2nd.}\ \underset{\text{Acrylic acid.}}{\left(C\left\{\begin{array}{l}H\\CH^{2\prime\prime}\\\hline O\\OH\end{array}\right.\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Formic acid.}}{\left(C\left\{\begin{array}{l}H\\O\\OH\end{array}\right.\right)} + \underset{\text{Acetic acid.}}{\left(C\left\{\begin{array}{l}CH^2+H\\O\\OH\end{array}\right.\right)} + \underset{\text{Hydrogen.}}{H^2}$$

The study of ethylcrotonic acid, the mode of production of which indicates its constitution, fortunately enables us to decide which of these equations is correct.

If this acid be supposed to be split up, according to the first or second of these hypotheses, it will be found to furnish in the first case a molecule of acetic acid and a molecule of butyric acid; and in the second case, two molecules of propionic acid:



$$\text{1st.}\ \underset{\text{Ethylcrotonic acid.}}{\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}C^2H^5\\C^2H^{4\prime\prime}\\\hline O\\OH\end{array}\right.\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Butyric acid.}}{\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}C^2H^5\\H^2\\\hline O\\OH\end{array}\right.\right)} + \underset{\text{Acetic acid.}}{\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H^3\\\hline O\\OH\end{array}\right.\right)} + \underset{\text{Hydrogen.}}{H^2}$$

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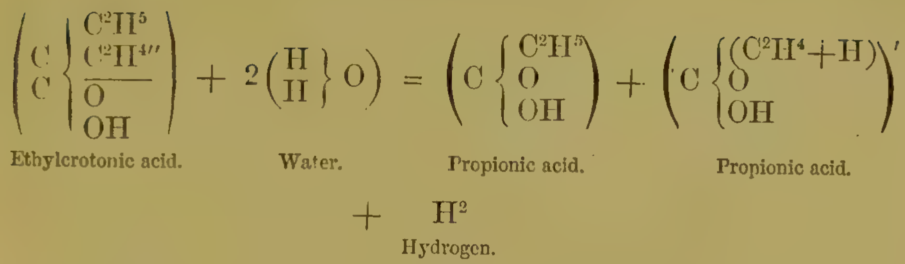
* For the sake of simplicity, we have supposed the hydration to take place directly with water instead of with potash. The reaction is the same in both cases: only with potash, instead of free acids potassic salts are produced.

2nd.

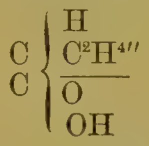


$$\underset{\text{Ethylcrotonic acid.}}{\left(\begin{array}{l}\mathrm{C}\\\mathrm{C}\end{array}\left\{\begin{array}{l}\mathrm{C^2H^5}\\\mathrm{C^2H^{4\prime\prime}}\\\hline\mathrm{O}\\\mathrm{OH}\end{array}\right.\right)} + \underset{\text{Water.}}{2\left(\begin{array}{l}\mathrm{H}\\\mathrm{H}\end{array}\right\}\mathrm{O}\Bigg)} = \underset{\text{Propionic acid.}}{\left(\mathrm{C}\left\{\begin{array}{l}\mathrm{C^2H^5}\\\mathrm{O}\\\mathrm{OH}\end{array}\right.\right)} + \underset{\text{Propionic acid.}}{\left(\mathrm{C}\left\{\begin{array}{l}\mathrm{(C^2H^4+H)^\prime}\\\mathrm{O}\\\mathrm{OH}\end{array}\right.\right)} + \underset{\text{Hydrogen.}}{\mathrm{H^2}}$$

Experiment having shown that it is a mixture of acetic and butyric acids which results when ethylcrotonic acid is treated by potash in fusion, it may be considered that the division most probably takes place in conformity with the first of these two hypotheses.

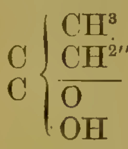
This reaction, once known, may serve to determine the constitution of the natural acids of the series $\mathrm{C^nH^{2n-2}O^2}$.

In fact, if we take the first homologue of acrylic acid, the acid ($\mathrm{C^4H^6O^2}$), we shall find it has two possible formulæ:



$$\begin{array}{l}\mathrm{C}\\\mathrm{C}\end{array}\left\{\begin{array}{l}\mathrm{H}\\\mathrm{C^2H^{4\prime\prime}}\\\hline\mathrm{O}\\\mathrm{OH}\end{array}\right.$$

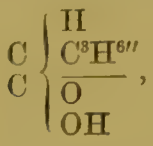
and



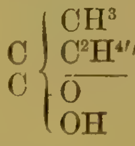
$$\begin{array}{l}\mathrm{C}\\\mathrm{C}\end{array}\left\{\begin{array}{l}\mathrm{CH^3}\\\mathrm{CH^{2\prime\prime}}\\\hline\mathrm{O}\\\mathrm{OH}\end{array}\right.$$

According to the first, it should be divided by potash into two molecules of acetic acid. According to the second, it should give a mixture of propionic and formic acids. As, in fact, crotonic acid gives acetic acid when heated with potash, while its artificial isomer gives a mixture of formic and propionic acids, the first of these two acids, crotonic acid, corresponds to the formula $\begin{array}{l}\mathrm{C}\\\mathrm{C}\end{array}\left\{\begin{array}{l}\mathrm{H}\\\mathrm{C^2H^{4\prime\prime}}\\\hline\mathrm{O}\\\mathrm{OH}\end{array}\right.$, and the other, methacrylic acid, to the formula $\begin{array}{l}\mathrm{C}\\\mathrm{C}\end{array}\left\{\begin{array}{l}\mathrm{CH^3}\\\mathrm{CH^{2\prime\prime}}\\\hline\mathrm{O}\\\mathrm{OH}\end{array}\right.$. This latter represents acrylic acid, of which a non-typical atom of hydrogen is replaced by methyl.

If we now pass to the second homologue of acrylic acid, we find three possible formulæ:

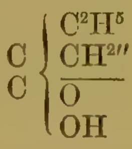


$$\begin{array}{l}\mathrm{C}\\\mathrm{C}\end{array}\left\{\begin{array}{l}\mathrm{H}\\\mathrm{C^3H^{6\prime\prime}}\\\hline\mathrm{O}\\\mathrm{OH}\end{array}\right.,$$



$$\begin{array}{l}\mathrm{C}\\\mathrm{C}\end{array}\left\{\begin{array}{l}\mathrm{CH^3}\\\mathrm{C^2H^{4\prime\prime}}\\\hline\mathrm{O}\\\mathrm{OH}\end{array}\right.$$

and



$$\begin{array}{l}\mathrm{C}\\\mathrm{C}\end{array}\left\{\begin{array}{l}\mathrm{C^2H^5}\\\mathrm{CH^{2\prime\prime}}\\\hline\mathrm{O}\\\mathrm{OH}\end{array}\right.$$

Of these three formulæ, the third must be rejected, because it does not account for the transformation of the known acids having this composition into acetic and propionic acids.

Of the two others, the second belongs to methylcrotonic acid, as is shown by the manner in which this acid is formed; only the first therefore can correspond to angelic acid.

The third homologue of acrylic acid may be represented by the four following formulæ:

$$\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H\\C^4H^{8\prime\prime}\\\hline O\\OH\end{array}\right., \quad \begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}CH^3\\C^3H^{6\prime\prime}\\\hline O\\OH\end{array}\right., \quad \begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}C^2H^5\\C^2H^{4\prime\prime}\\\hline O\\OH\end{array}\right., \quad \begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}C^3H^7\\CH^{2\prime\prime}\\\hline O\\OH\end{array}\right.$$

The mode of decomposition by potash of the known acids thus composed excludes the second and fourth of these rational formulæ. Acetic and butyric acids are formed in this decomposition, while according to these formulæ there ought to be formed either propionic acid alone, or a mixture of valeric and formic acids. Of the two formulæ which remain, one $\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}C^2H^5\\C^2H^{4\prime\prime}\\\hline O\\OH\end{array}\right.\right)$ belongs to the synthetical acid; the other $\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H\\C^4H^{8\prime\prime}\\\hline O\\OH\end{array}\right.\right)$ is that of its isomer, pyroterebic acid.

Sixteen formulæ would be possible for oleic acid, but of these only two would coincide with the decomposition which this acid undergoes under the influence of potash; these are:

$$\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H\\C^{16}H^{32\prime\prime}\\\hline O\\OH\end{array}\right. \quad \text{and} \quad \begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}C^{14}H^{29}\\C^2H^{4\prime\prime}\\\hline O\\OH\end{array}\right.$$

It is impossible to decide between these formulæ, Frankland not having obtained synthetically any acid of the same composition as oleic acid which can be compared to it. But the natural acids of this series having each a single radicle of alcohol in their molecule, the first formula is the most probable.

There remains campholic acid ($C^{10}H^{18}O^2$). But this has such different properties from the acids just reviewed, that it should not be placed in the same class. It appears to be much more completely saturated.

On reviewing the preceding remarks, it may be asked if, where 2, 3 . . . *n* formulæ are said to be possible, there may not sometimes be a greater number.

Thus, besides the two formulæ of angelic and methylcrotonic acids,

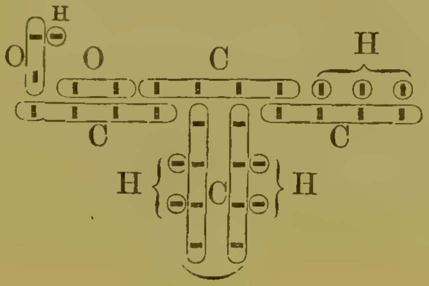
$$\underset{\text{Angelic acid.}}{\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H\\C^3H^{6\prime\prime}\\\hline O\\OH\end{array}\right.} \quad \text{and} \quad \underset{\text{Methylcrotonic acid.}}{\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}CH^3\\C^2H^{4\prime\prime}\\\hline O\\OH\end{array}\right.}$$

there appears to be a third possible:

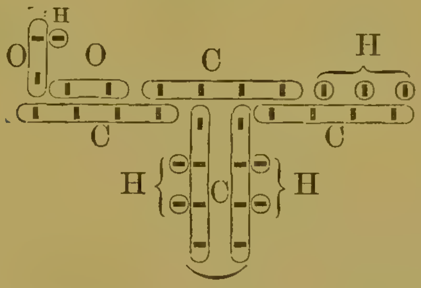
$$\begin{matrix}C\\C\\C\end{matrix}\left\{\begin{array}{l}H^3\\\hline C^2H^{4''}\\\hline O\\OH\end{array}\right.$$

But this formula would be precisely the same as that of methylcrotonic acid. This will be seen by translating the two into molecular designs:

$$\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}CH^3\\C^2H^{4''}\\\hline O\\OH\end{array}\right. =$$



$$\begin{matrix}C\\C\\C\end{matrix}\left\{\begin{array}{l}H^3\\\hline C^2H^{4''}\\\hline O\\OH\end{array}\right. =$$



Acrylic acid and its natural homologues correspond to the formulæ:

$$\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H\\CH^{2''}\\\hline O\\OH\end{array}\right., \quad \begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H\\C^2H^{4''}\\\hline O\\OH\end{array}\right., \quad \begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H\\C^3H^{6''}\\\hline O\\OH\end{array}\right. \ldots \text{etc.}$$

They have a very simple relation with acetic acid, each of them being derived from that acid by the substitution of a radicle $CH^2$, $C^2H^{4''}$, $C^3H^{6''}$, etc., for $H^2$. It is therefore probable that they would be obtained by causing the bihydrobromic ethers of the different glycols to act on bisodacetic ether:

$$\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H\\Na^2\\\hline O\\OC^2H^5\end{array}\right.\right) + (C^2H^{4''}Br^2) = 2\left(\begin{matrix}Na\\Br\end{matrix}\right\}\right) + \left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H\\C^2H^{4''}\\\hline O\\OH\end{array}\right.\right)$$

Bisodacetic ether. Bromide of ethylene. Bromide of sodium. Crotonic acid.

The artificial acids of this series might also be obtained by this process, on substituting the homologues of acetic acid for the acid itself:

$$\underset{\text{Bisodopropionic ether.}}{\begin{matrix}\mathrm{C}\\\mathrm{C}\end{matrix}\left\{\begin{array}{l}CH^3\\Na^2\\ \hline O\\OC^2H^5\end{array}\right.} + \underset{\text{Bromide of ethylene.}}{\left(\left.\begin{matrix}C^2H^{4''}\\Br^2\end{matrix}\right\}\right)} = \underset{\text{Bromide of sodium.}}{2\left(\left.\begin{matrix}Na\\Br\end{matrix}\right\}\right)} = \underset{\text{Methylcrotonic acid.}}{\left(\begin{matrix}\mathrm{C}\\\mathrm{C}\end{matrix}\left\{\begin{array}{l}CH^3\\C^2H^{4''}\\ \hline O\\OH\end{array}\right.\right)}$$

## ACIDS OF THE SERIES $C^nH^{2n-10}O^2$.

Only one acid of this series, cinnamic acid ($C^9H^8O^2$), is known. It is found ready formed in certain natural balsams, and is also obtained by oxidizing its aldehyd, the essential oil of cinnamon. It has been prepared synthetically by two processes.

*First.*—Oil of bitter almonds is heated with chloride of benzoyl in a closed vessel; hydrochloric acid is disengaged and cinnamic acid is formed:

$$\underset{\text{Benzoic aldehyd.}}{(C^7H^6O)} + \underset{\text{Chloride of acetyl.}}{\left(\left.\begin{matrix}C^2H^3O\\Cl\end{matrix}\right\}\right)} = \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}} + \underset{\text{Cinnamic acid.}}{(C^9H^8O^2)}$$

*Second Process.*—Chloracetene is made to act on benzoate of potassium:

$$\underset{\text{Benzoate of potassium.}}{\left(\left.\begin{matrix}C^7H^5O\\K\end{matrix}\right\}O\right)} + \underset{\text{Chloracetene.}}{(C^2H^3Cl)} = \underset{\text{Potassic chloride.}}{\left.\begin{matrix}K\\Cl\end{matrix}\right\}} + \underset{\text{Cinnamic acid.}}{(C^9H^8O^2)}$$

The chloracetene used in this preparation is produced by the reaction of chloride of carbonyl on ordinary aldehyd:

$$\underset{\text{Aldehyd.}}{(C^2H^4O)} + \underset{\text{Chloride of carbonyl.}}{(CO''Cl^2)} = \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}} + \underset{\text{Carbonic anhydride.}}{(CO^2)} + \underset{\text{Chloracetene.}}{(C^2H^3Cl)}$$

It may be presumed that on substituting another alkaline salt for benzoate of potassium, other acids of the same or of a different series might be obtained by the same process.

Properties.—1st. Cinnamic acid fixes directly two molecules of bromine, and gives an acid which, under the influence of nascent hydrogen, is transformed into a new acid of the benzoic series:

$$\underset{\text{Cinnamic acid.}}{(C^9H^8O^2)} + \underset{\text{Bromine.}}{Br^2} = \underset{\text{Bibromoxylenic acid.}}{(C^9H^8Br^2O^2)}$$

$$\underset{\text{Bibromoxylenic acid.}}{(C^9H^8Br^2O^2)} + \underset{\text{Hydrogen.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}\right)} = \underset{\text{Hydrobromic acid.}}{2\left(\left.\begin{matrix}H\\Br\end{matrix}\right\}\right)} + \underset{\text{Xylenic acid.}}{(C^9H^{10}O^2)}$$

2nd. This xylenic acid is also produced by the direct action of nascent hydrogen on cinnamic acid.

3rd. Potash in the state of fusion transforms cinnamic acid into a mixture of acetic and benzoic acids:

$$\underset{\text{Cinnamic acid.}}{(C^{9}H^{8}O^{2})} + \underset{\text{Potash.}}{2(KHO)} = \underset{\text{Potassic acetate.}}{(C^{2}H^{3}KO^{2})} + \underset{\text{Benzoate of potassium.}}{(C^{7}H^{5}KO^{2})} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}}$$

Cinnamic acid therefore appears to act the same part in the aromatic series as acrylic acid acts in the series of the fatty acids.

In the methods of preparation just described, the acids are sometimes obtained in the state of salts, but nothing is easier than to obtain a free acid when we have one of its salts. If the acid be volatile, its salt only requires to be distilled with sulphuric acid. If the acid be not volatile, it is transformed into a salt of lead, which is treated with sulphuretted hydrogen and water; sulphide of lead is formed which is separated by filtration, and the acid set free is dissolved and obtained from the solution by evaporation. The preparation of the salt of lead is very easy. Its salts of fixed acids are in reality almost all insoluble, and are obtained by means of double decomposition, by mixing solutions of a soluble salt and acetate of lead.

**Monatomic Acids actually known.**—These acids are :—

1st. *In the series* $C^{n}H^{2n}O^{2}$ :

| | | | |
|---|---|---|---|
| Formic acid, | $C\ H^{2}\ O^{2}$, | corresponding to methylic alcohol, | $C\ H^{4}\ O$. |
| Acetic acid, | $C^{2}\ H^{4}\ O^{2}$, | corresponding to ethylic alcohol, | $C^{2}\ H^{6}\ O$. |
| Propionic acid, | $C^{3}\ H^{6}\ O^{2}$, | corresponding to propylic alcohol, | $C^{3}\ H^{8}\ O$. |
| Butyric acid, | $C^{4}\ H^{8}\ O^{2}$, | corresponding to butylic alcohol, | $C^{4}\ H^{10}O$. |
| Valeric acid, | $C^{5}\ H^{10}O^{2}$, | corresponding to amylic alcohol, | $C^{5}\ H^{12}O$. |
| Caproic acid, | $C^{6}\ H^{12}O^{2}$, | corresponding to hexylic alcohol, | $C^{6}\ H^{14}O$. |
| Œnanthylic acid, | $C^{7}\ H^{14}O^{2}$, | corresponding to heptylic alcohol, | $C^{7}\ H^{16}O$. |
| Caprylic acid, | $C^{8}\ H^{16}O^{2}$, | corresponding to octylic alcohol, | $C^{8}\ H^{18}O$. |
| Pelargonic acid, | $C^{9}\ H^{18}O^{2}$, | corresponding to nonylic alcohol, | $C^{9}\ H^{20}O$*. |
| Rutic acid, | $C^{10}H^{20}O^{2}$, | corresponding to decylic alcohol, | $C^{10}H^{22}O$*. |
| Lauric acid, | $C^{12}H^{24}O^{2}$, | corresponding to dodecylic alcohol, | $C^{12}H^{26}O$*. |
| Cocinic acid, | $C^{13}H^{26}O^{2}$, | corresponding to tridecylic alcohol, | $C^{13}H^{28}O$*. |
| Myristic acid, | $C^{14}H^{28}O^{2}$, | corresponding to tetradecylic alcohol . . . . . . . . | $C^{14}H^{30}O$*. |
| Benic acid, | $C^{15}H^{30}O^{2}$ ?, | corresponding to pentadecylic alcohol . . . . . . . . | $C^{16}H^{32}O$*. |
| Palmitic acid, | $C^{16}H^{32}O^{2}$, | corresponding to cetylic alcohol, | $C^{16}H^{34}O$. |
| Margaric acid, | $C^{17}H^{34}O^{2}$ ?, | corresponding to heptadecylic alcohol . . . . . . . . | $C^{17}H^{36}O$*. |
| Stearic acid, | $C^{18}H^{36}O^{2}$, | corresponding to octodecylic alcohol . . . . . . . . | $C^{18}H^{38}O$*. |
| Arachidic acid, | $C^{20}H^{40}O^{2}$, | corresponding to the alcohol | $C^{20}H^{42}O^{2}$*. |
| Cerotic acid, | $C^{27}H^{54}O^{2}$, | corresponding to cerylic alcohol, | $C^{27}H^{56}O$. |
| Melissic acid, | $C^{30}H^{60}O^{2}$, | corresponding to myricic alcohol, | $C^{30}H^{62}O$. |

Those alcohols marked with an asterisk are not yet known, though their acids have been obtained, and a note of interrogation is placed after benic and margaric acids, because benic acid is far from being known with certainty, and, according to Heinz, the body hitherto called margaric acid is a mixture of palmitic and stearic acids.

2nd. *In the series* $C^nH^{2n-2}O^2$:

Acrylic acid $C^3H^4O^2$, corresponding to allylic alcohol, $C^3H^6O$.

Crotonic acid and its isomer, methacrylic acid, $C^4H^6O^2$, corresponding to two isomeric alcohols, $C^4H^8O$*.

Angelic acid and its isomer, methylcrotonic acid, $C^5H^8O^2$, corresponding to two isomeric alcohols, $C^5H^{10}O$*.

Pyroterebic acid and its isomer, ethylcrotonic acid, $C^6H^{10}O^2$, corresponding to two isomeric alcohols, $C^6H^{12}O^2$*.

Campholic acid, $C^{10}H^{18}O^2$, corresponding to mentholic alcohol, $C^{10}H^{20}O$.

Oleic acid, $C^{18}H^{34}O^2$, corresponding to oleic alcohol, $C^{18}H^{36}O$*.

3rd. *In the series* $C^nH^{2n-4}O^2$:

Sorbic and parasorbic acids, $C^6H^8O^2$, corresponding to two isomeric alcohols, $C^6H^{10}O$*.

Camphic acid, $C^{10}H^{16}O^2$, corresponding to campholic alcohol (borneol), $C^{10}H^{18}O$.

4th. *In the series* $C^nH^{2n-6}O^2$:

Hydrobenzoic acid, $C^7H^8O^2$, corresponding to the alcohol $C^7H^{10}O^2$*.

5th. *In the series* $C^nH^{2n-8}O^2$:

Benzoic acid, $C^7H^6O^2$, corresponding to benzilic alcohol, $C^7H^8O$.

Toluic and alphatoluic acids, $C^8H^8O^2$, corresponding to tollylic alcohol, $C^8H^{10}O$, and to a second unknown alcohol of the same composition.

Xylenic and alphaxylenic acids, $C^9H^{10}O^2$, corresponding to two isomeric alcohols, $C^9H^{12}O$*.

Cuminic acid, $C^{10}H^{12}O^2$, corresponding to cumylic alcohol, $C^{10}H^{14}O$.

Alphacymenic acid, $C^{11}H^{14}O^2$, corresponding to cymelic alcohol, $C^{11}H^{16}O$*.

6th. *In the series* $C^nH^{2n-10}O^2$:

Cinnamic acid and its isomer, atropic acid, $C^9H^8O^2$, corresponding to cinnamic alcohol, $C^9H^{10}O$, and to an unknown isomer of this alcohol.

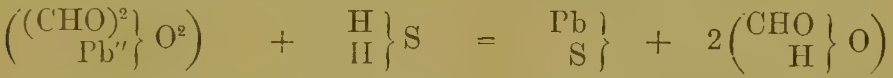
## Study of the best-known Monatomic Acids.

**Formic Acid.**—Preparation.—Several processes have been used for the preparation of formic acid. It is generally produced when organic substances are oxidized. This acid is now usually prepared by decomposing oxalic acid by means of glycerine, which, by a catalytic action, causes oxalic acid to split up into formic acid and carbonic anhydride without itself being altered:

$$\underset{\text{Oxalic acid.}}{(C^2H^2O^4)} = \underset{\text{Carbonic anhydride.}}{CO^2} + \underset{\text{Formic acid.}}{(CH^2O^2)}.$$

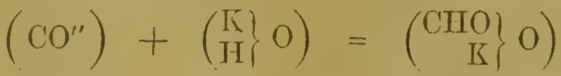
A solution of oxalic acid in water is added to glycerine and distilled. When a certain quantity of liquid has passed over, more of the solution of oxalic acid is again poured into the retort containing the glycerine, and the operation is thus continued for an indefinite period.

In order to obtain normal formic acid ($CH^2O^2$) entirely free from water, the distilled acid liquids are saturated with oxide of lead, evaporated to dryness, and the formiate of lead is well dried. It is then placed in a glass tube, which is heated in a sand-bath and through which a current of dry sulphuretted hydrogen is transmitted. Sulphide of lead and pure formic acid are produced. The latter distils over and is collected in a cold receiver:



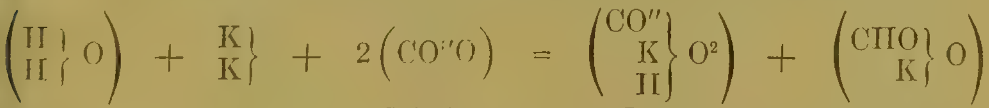
$$\underset{\text{Formiate of lead.}}{\left(\left.\begin{matrix}(CHO)^2\\ Pb''\end{matrix}\right\}O^2\right)} + \underset{\text{Sulphuretted hydrogen.}}{\left.\begin{matrix}H\\ H\end{matrix}\right\}S} = \underset{\text{Sulphide of lead.}}{\left.\begin{matrix}Pb\\ S\end{matrix}\right\}} + \underset{\text{Formic acid.}}{2\left(\left.\begin{matrix}CHO\\ H\end{matrix}\right\}O\right)}$$

Berthelot has prepared formic acid synthetically by heating oxide of carbon with potash. By the union of these bodies, potassic formiate is formed, which by distillation with dilute sulphuric acid furnishes dilute formic acid, from which the pure acid is extracted as before:



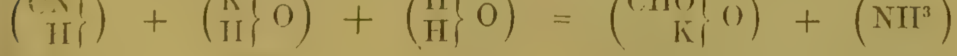
$$\underset{\text{Oxide of carbon.}}{\left(CO''\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\ H\end{matrix}\right\}O\right)} = \underset{\text{Potassic formiate.}}{\left(\left.\begin{matrix}CHO\\ K\end{matrix}\right\}O\right)}$$

Kolbe has also obtained the formiate of potassium by transmitting a current of carbonic anhydride and vapour of water over potassium:



$$\underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)} + \underset{\text{Potassium.}}{\left.\begin{matrix}K\\ K\end{matrix}\right\}} + \underset{\text{Carbonic anhydride.}}{2\left(CO''O\right)} = \underset{\text{Potassic bicarbonate.}}{\left(\left.\begin{matrix}CO''\\ K\\ H\end{matrix}\right\}O^2\right)} + \underset{\text{Potassic formiate.}}{\left(\left.\begin{matrix}CHO\\ K\end{matrix}\right\}O\right)}$$

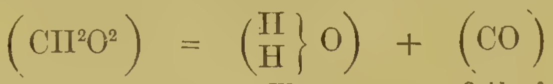
Potassic formiate is also obtained by heating hydrocyanic acid with an excess of a solution of potash in alcohol:



$$\underset{\text{Hydrocyanic acid.}}{\left(\left.\begin{matrix}CN\\ H\end{matrix}\right\}\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\ H\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)} = \underset{\text{Potassic formiate.}}{\left(\left.\begin{matrix}CHO\\ K\end{matrix}\right\}O\right)} + \underset{\text{Ammonia.}}{\left(NH^3\right)}$$

This latter reaction is entirely analogous to that which gives the homologues of formic acid by means of the hydrocyanic ethers and potash. Water may in reality be considered as the first term in the series of the alcohols ($C^nH^{2n+2}O$), for on taking away $CH^2$ from methylic alcohol $CH^4O$, there remains $H^2O$, which enters into the general formula, if in this latter $n$ is made to equal 0. Hence hydrocyanic acid is similar to a cyanhydric ether, and ought, like these bodies, under the influence of alkalies, to give the acid which corresponds to the first homologue of water, methylic alcohol.

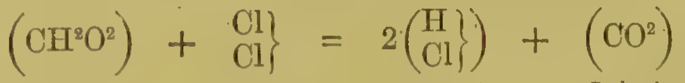
PROPERTIES.—1st. Bodies having great affinity for water, like sulphuric acid, decompose formic acid, disengaging oxide of carbon :



$$\left(CH^2O^2\right) = \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + \left(CO\right)$$

Formic acid. Water. Oxide of carbon.

2nd. Chlorine and bromine take the hydrogen from formic acid, but they are not substituted for it, as is the case in the higher homologues of this acid. The molecule is entirely destroyed, and a mixture of hydrochloric or hydrobromic acid gases and carbonic anhydride is disengaged :

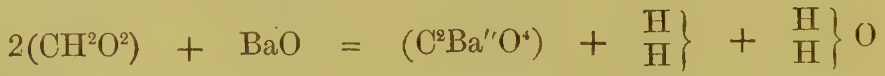


$$\left(CH^2O^2\right) + \left.\begin{matrix}Cl\\Cl\end{matrix}\right\} = 2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right) + \left(CO^2\right)$$

Formic acid. Chlorine. Hydrochloric acid. Carbonic anhydride.

3rd. Oxidizing agents give rise to a similar reaction. They seize the hydrogen of formic acid to form water, and carbonic anhydride is disengaged. Formic acid has such a tendency to undergo this decomposition that it acts as a reducing agent. Thus, when heated with nitrate of mercury or of silver, it reduces these salts, precipitating the metal.

4th. Under the influence of powerful bases, formic acid is transformed into oxalic acid, disengaging hydrogen :



$$2(CH^2O^2) + BaO = (C^2Ba''O^4) + \left.\begin{matrix}H\\H\end{matrix}\right\} + \left.\begin{matrix}H\\H\end{matrix}\right\}O$$

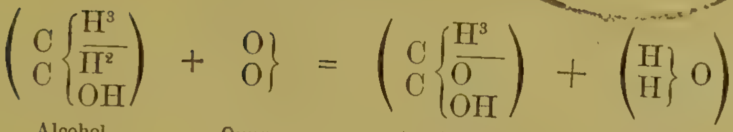
Formic acid. Baryta. Oxalic acid. Hydrogen. Water.

If too great heat were applied during this process, the oxalate itself would be transformed into carbonate, with disengagement of carbonic oxide.

As oxalic acid may be transformed by the action of nascent hydrogen into glycolic acid, which readily furnishes acetic acid, the reaction of powerful bases on formic acid is a means of transition from the formic to the acetic series.

**Acetic Acid** $\left(\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O\right)$.—PREPARATION.—1st. Acetic acid diluted with water constitutes the essential part of vinegar. It is formed by the oxidation of the alcohol contained in wine :

MEDICINE



$$\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\H^2\\OH\end{matrix}\right.\right) + \left.\begin{matrix}O\\O\end{matrix}\right\} = \left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\O\\OH\end{matrix}\right.\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

Alcohol. Oxygen. Acetic acid. Water.

Acetic acid is also produced in great quantities by the dry distillation of several organic substances, especially of wood, and it is in this manner that the greater part of the acid used in manufactures is obtained.

To transform pure alcohol into acetic acid, platinum black must be used, but when the alcohol is diluted it acetifies much more readily. Pasteur has of late years discovered that, contrary to the general opinion, the transformation of wine into vinegar is not merely owing to the action of air, but to the influence of a particular ferment long known as mother of vinegar. At Orleans, where vinegar is manufactured in large quantities, the wine is allowed to run through vats full of beech chips. These chips increase the surface exposed to the air, and in this way aid the oxidation of the alcoholic liquid. But the acetification only takes place when they are covered with mother of vinegar; therefore, when a new apparatus is used, the chips must first be steeped in vinegar charged with ferment.

When the vinegar is distilled, the acetic acid is freed from the foreign substances it held in solution, but is obtained very diluted. In order to procure it at its maximum concentration, the diluted acid must be saturated by a base, potassium or sodium, and evaporated to dryness; then the acetate is fused to drive off the last traces of moisture, and finally distilled with sulphuric acid. To free the distilled liquid from the small quantity of sulphuric acid it may have carried over, it is shaken with very dry acetate of barium and again distilled.

The acetic acid thus prepared is still not entirely freed from water; in order to effect this, it must be congealed by means of a freezing mixture, and then allowed to resume its liquid state, the portions of acid which are first liquefied being rejected. After undergoing this process two or three times, it is entirely pure.

The same method is used to extract acetic acid from the products of the distillation of wood. But before decomposing the acetate of sodium by sulphuric acid, this salt should be gently roasted, so as to destroy oreign matters without altering itself. The salt must then be crystalized.

Vœlckel has modified the method of extracting acetic acid from the roducts of the distillation of wood. He saturates these products by ime without rectifying them. Certain resinous substances are sepa-ated, while others remain in the solution along with the acetate of alcium, and colour it a deep brown. He then filters the liquid, educes it to half its volume by evaporation in a brass dish, and adds nough hydrochloric acid to give it a persistent acid reaction: 2 or 3 ilogrammes of acid are generally sufficient for 150 litres of vinegar.

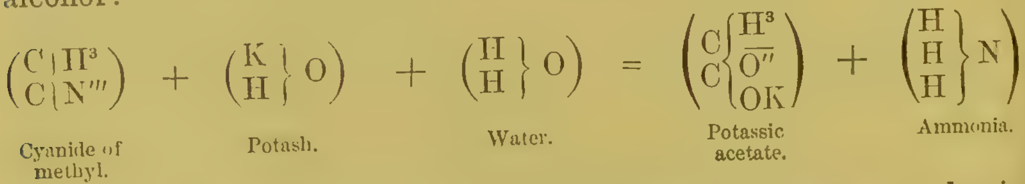
The resins which were in solution are thereby separated, and removed. He continues to boil the liquid, in order to drive off certain volatile substances, such as creosote, which are set free at the same time as these resins, and then dries thoroughly the acetate of calcium, after which it is distilled with hydrochloric acid (90 to 95 parts of hydrochloric acid of a density of 1·16, for 100 p. of the acetate). To remove any hydrochloric acid which may have passed over during the distillation, the product is rectified with potassic bichromate. This also destroys a foreign substance which communicates a peculiar odour to the acetic acid.

The acetic acid thus obtained though strong enough for the ordinary requirements of commerce is still considerably diluted. To concentrate it, it must be transformed into a salt of sodium, and then submitted to the process already described.

Formerly, a highly-concentrated acid was obtained in pharmacy by submitting the acetate of copper (or lead) to dry distillation. But a part of the copper passes to the state of sub-acetate and crystallizes in the neck of the retort, a portion of this is carried over by the acid which distils, then it absorbs oxygen and is converted into per-acetate, colouring the acid blue. It is therefore necessary to rectify the acetic acid obtained by this process a second time.

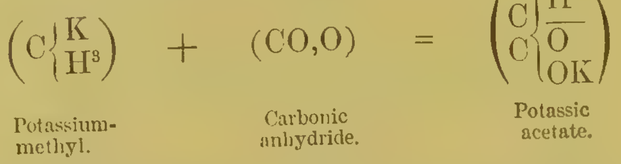
Besides the ordinary method of preparation already described, and which alone is used in manufactures, there exist other methods of preparing acetic acid, which are all synthetical.

1st. Acetate of potassium, and consequently acetic acid, may be prepared by boiling cyanide of methyl with an alcoholic solution of potash, until all disengagement of ammonia ceases, and then evaporating the alcohol:



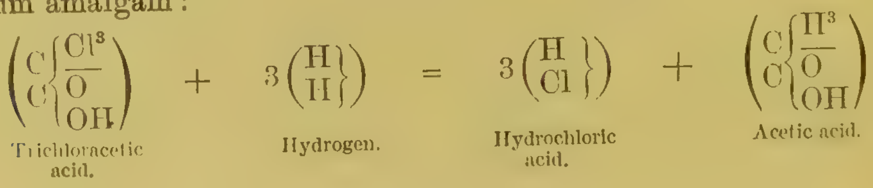
$$\underset{\text{Cyanide of methyl.}}{\left(\begin{matrix}C\,|\,H^3\\ C\,|\,N'''\end{matrix}\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\ H\end{matrix}\right\} O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\} O\right)} = \underset{\text{Potassic acetate.}}{\left(\begin{matrix}C\\ C\end{matrix}\left\{\begin{matrix}H^3\\ \overline{O''}\\ OK\end{matrix}\right.\right)} + \underset{\text{Ammonia.}}{\left(\left.\begin{matrix}H\\ H\\ H\end{matrix}\right\} N\right)}$$

2nd. Potassic acetate may also be prepared by causing carbonic anhydride to act on potassium-methyl:



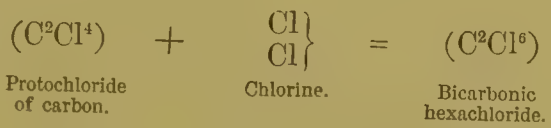
$$\underset{\text{Potassium-methyl.}}{\left(C\left\{\begin{matrix}K\\ H^3\end{matrix}\right.\right)} + \underset{\text{Carbonic anhydride.}}{(CO,O)} = \underset{\text{Potassic acetate.}}{\left(\begin{matrix}C\\ C\end{matrix}\left\{\begin{matrix}H^3\\ \overline{O}\\ OK\end{matrix}\right.\right)}$$

3rd. Melsens has obtained acetic acid by submitting trichloracetic acid to the action of nascent hydrogen, disengaged from water by sodium amalgam:

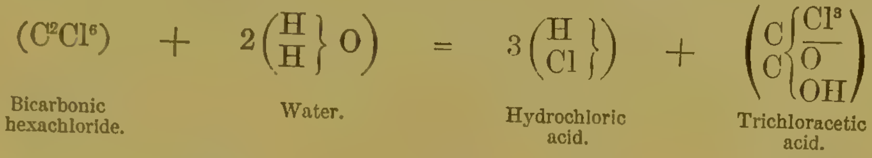


$$\underset{\text{Trichloracetic acid.}}{\left(\begin{matrix}C\\ C\end{matrix}\left\{\begin{matrix}Cl^3\\ \overline{O}\\ OH\end{matrix}\right.\right)} + \underset{\text{Hydrogen.}}{3\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}\right)} = \underset{\text{Hydrochloric acid.}}{3\left(\left.\begin{matrix}H\\ Cl\end{matrix}\right\}\right)} + \underset{\text{Acetic acid.}}{\left(\begin{matrix}C\\ C\end{matrix}\left\{\begin{matrix}H^3\\ \overline{O}\\ OH\end{matrix}\right.\right)}$$

This method is synthetical, since Kolbe has succeeded in preparing trichloracetic acid by causing water and chlorine to act simultaneously on the chloride of carbon ($C^2Cl^4$). This latter reaction takes place in two stages: in the first, this chloride absorbs $Cl^2$, and passes to the state of bicarbonic hexachloride ($C^2Cl^6$); in the second, this latter body is transformed into hydrochloric and trichloracetic acids:

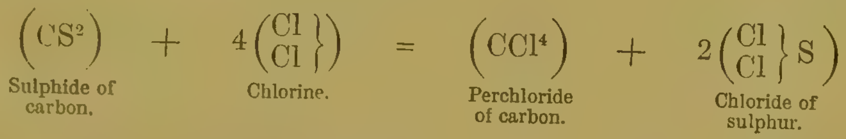


$$\underset{\text{Protochloride of carbon.}}{(C^2Cl^4)} + \underset{\text{Chlorine.}}{\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}} = \underset{\text{Bicarbonic hexachloride.}}{(C^2Cl^6)}$$



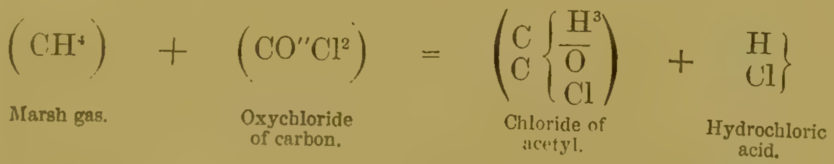
$$\underset{\text{Bicarbonic hexachloride.}}{(C^2Cl^6)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Hydrochloric acid.}}{3\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Trichloracetic acid.}}{\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}Cl^3\\ \overline{O}\\OH\end{matrix}\right.\right)}$$

The protochloride of carbon ($C^2Cl^4$) is produced when the perchloride ($CCl^4$) is transmitted through a red-hot tube, and the perchloride ($CCl^4$) is formed by the reaction of dry chlorine on the sulphide of carbon:

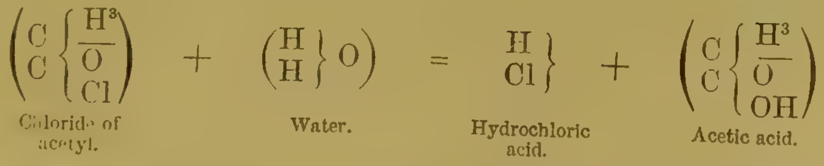


$$\underset{\text{Sulphide of carbon.}}{(CS^2)} + \underset{\text{Chlorine.}}{4\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}\right)} = \underset{\text{Perchloride of carbon.}}{(CCl^4)} + \underset{\text{Chloride of sulphur.}}{2\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}S\right)}$$

4th. Harnitz-Harnitzky has obtained the chloride of acetyl, and consequently acetic acid, by causing marsh gas to act on the oxychloride of carbon:



$$\underset{\text{Marsh gas.}}{(CH^4)} + \underset{\text{Oxychloride of carbon.}}{(CO''Cl^2)} = \underset{\text{Chloride of acetyl.}}{\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\ \overline{O}\\Cl\end{matrix}\right.\right)} + \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}}$$



$$\underset{\text{Chloride of acetyl.}}{\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\ \overline{O}\\Cl\end{matrix}\right.\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}} + \underset{\text{Acetic acid.}}{\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\ \overline{O}\\OH\end{matrix}\right.\right)}$$

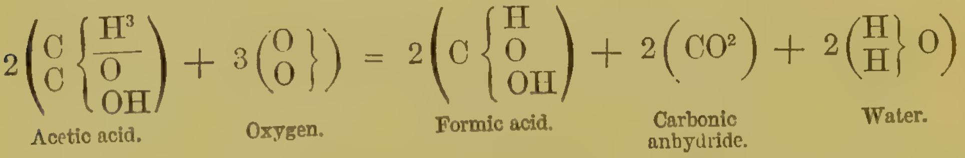
PROPERTIES.—Concentrated acetic acid crystallizes at +17° in brilliant transparent plates, but it loses this property if a small quantity of water be added; above 17° it is a colourless transparent liquid of a lensity of 1·064, having a strong odour of vinegar and a very acid aste. It is sufficiently corrosive to cause a blister when applied to he skin.

It boils at 120°; its vapour density taken between 219° and 239° ias been found by Cahours to be from 2·12 to 2·7, but it is greater at lower temperature; it diminishes gradually towards 219°, where it ecomes constant.

Acetic acid absorbs moisture from the atmosphere, and mixes in all proportions with water and alcohol; if water be added to it, its density at first increases, but diminishes if the dilution be continued. Its maximum density is 1·073. It corresponds to the hydrate $(C^2H^4O^2)+aq.$ and boils at 104°.

The vapour of acetic acid is inflammable, and burns with a beautiful blue flame.

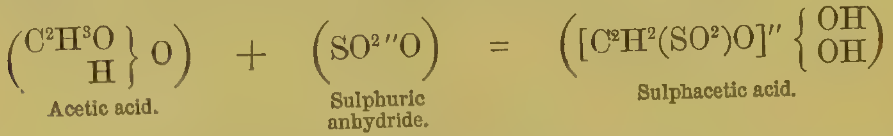
This acid dissolves camphor, the resins, fibrin, coagulated albumen, and several other substances. Phosphorus is slightly soluble in it. Nitric acid does not attack it. Periodic acid converts it into formic acid and carbonic anhydride, and itself passes to the state of iodic acid, or even of free iodine. This is merely an instance of oxidation.



$$2\left(\begin{array}{l}\mathrm{C}\\\mathrm{C}\end{array}\left\{\begin{array}{l}\mathrm{H^3}\\\hline\mathrm{O}\\\mathrm{OH}\end{array}\right.\right)+3\left(\left.\begin{array}{c}\mathrm{O}\\\mathrm{O}\end{array}\right\}\right)=2\left(\mathrm{C}\left\{\begin{array}{l}\mathrm{H}\\\mathrm{O}\\\mathrm{OH}\end{array}\right.\right)+2\left(\mathrm{CO^2}\right)+2\left(\left.\begin{array}{c}\mathrm{H}\\\mathrm{H}\end{array}\right\}\mathrm{O}\right)$$

Acetic acid. Oxygen. Formic acid. Carbonic anhydride. Water.

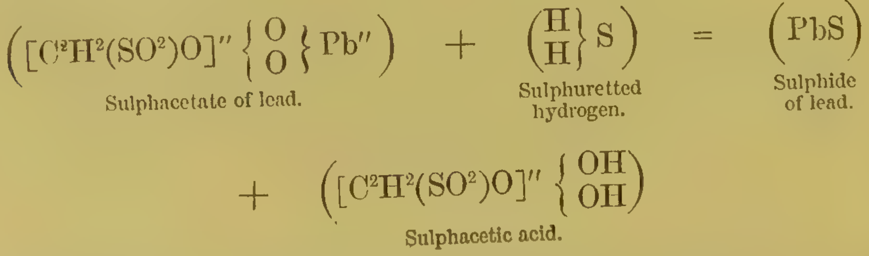
When a mixture of acetic and concentrated sulphuric acids is heated, it turns black, and sulphurous and carbonic anhydrides are disengaged. When, instead of ordinary concentrated sulphuric acid, disulphuric (Nordhausen) acid is employed, the mixture becomes heated spontaneously, and if the temperature be further raised, carbonic anhydride, almost free from sulphurous anhydride, is disengaged. When sulphuric anhydride is thrown into crystallizable acetic acid, and the mixture is heated for some time to 75°, sulphacetic acid is obtained:



$$\left(\left.\begin{array}{r}\mathrm{C^2H^3O}\\\mathrm{H}\end{array}\right\}\mathrm{O}\right)+\left(\mathrm{SO^{2}}''\mathrm{O}\right)=\left([\mathrm{C^2H^2(SO^2)O}]''\left\{\begin{array}{l}\mathrm{OH}\\\mathrm{OH}\end{array}\right.\right)$$

Acetic acid. Sulphuric anhydride. Sulphacetic acid.

This acid is isolated by diluting the liquid with water, saturating with carbonate of lead, and filtering. The excess of sulphuric anhydride passes into sulphuric acid, and is then precipitated in the state of sulphate of lead, while the sulphacetate of lead remains in solution. It may either be crystallized or be used for the preparation of sulphacetic acid by submitting it to the action of a current of sulphuretted hydrogen:



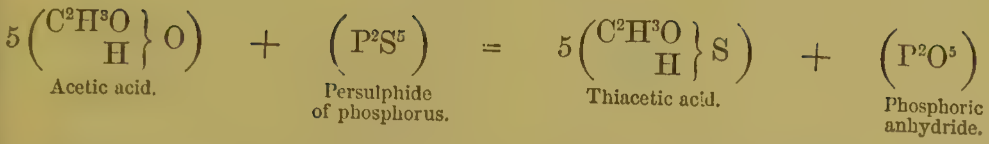
$$\left([\mathrm{C^2H^2(SO^2)O}]''\left\{\begin{array}{c}\mathrm{O}\\\mathrm{O}\end{array}\right\}\mathrm{Pb}''\right)+\left(\left.\begin{array}{c}\mathrm{H}\\\mathrm{H}\end{array}\right\}\mathrm{S}\right)=\left(\mathrm{PbS}\right)$$

Sulphacetate of lead. Sulphuretted hydrogen. Sulphide of lead.

$$+\left([\mathrm{C^2H^2(SO^2)O}]''\left\{\begin{array}{l}\mathrm{OH}\\\mathrm{OH}\end{array}\right.\right)$$

Sulphacetic acid.

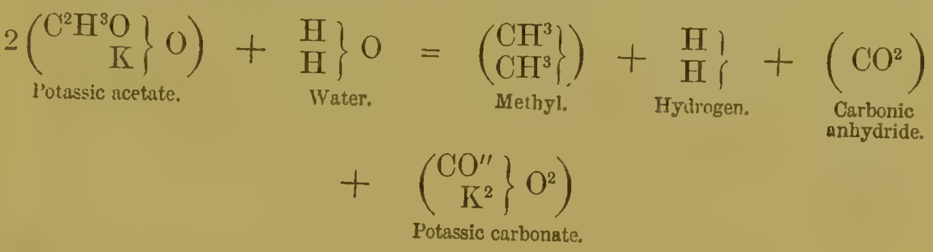
The persulphide of phosphorus transforms acetic acid into thiacetic acid:



$$\underset{\text{Acetic acid.}}{5\left(\left.\begin{array}{r}C^2H^3O\\ H\end{array}\right\}O\right)} + \underset{\text{Persulphide of phosphorus.}}{\left(P^2S^5\right)} = \underset{\text{Thiacetic acid.}}{5\left(\left.\begin{array}{r}C^2H^3O\\ H\end{array}\right\}S\right)} + \underset{\text{Phosphoric anhydride.}}{\left(P^2O^5\right)}$$

Chlorine can be substituted for one, two, or three atoms of the hydrogen of acetic acid. For this substitution to take place readily, the operation must be conducted in the sunlight. Bromine also acts in the same manner, but only when heated with the acid to a high temperature in hermetically-sealed tubes.

Acetic acid is a bad conductor of electricity, but the acetate of potassium is decomposed by galvanism, and methyl is formed:

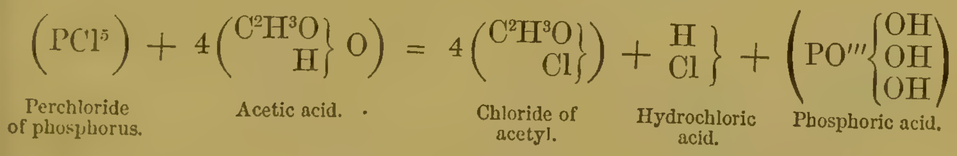


$$\underset{\text{Potassic acetate.}}{2\left(\left.\begin{array}{r}C^2H^3O\\ K\end{array}\right\}O\right)} + \underset{\text{Water.}}{\left.\begin{array}{r}H\\ H\end{array}\right\}O} = \underset{\text{Methyl.}}{\left(\left.\begin{array}{r}CH^3\\ CH^3\end{array}\right\}\right)} + \underset{\text{Hydrogen.}}{\left.\begin{array}{r}H\\ H\end{array}\right\}} + \underset{\text{Carbonic anhydride.}}{\left(CO^2\right)}$$

$$+ \underset{\text{Potassic carbonate.}}{\left(\left.\begin{array}{r}CO''\\ K^2\end{array}\right\}O^2\right)}$$

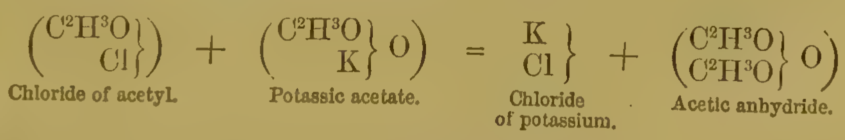
When the acetate of potassium is distilled with arsenious anhydride, a fœtid and very inflammable oil passes over. This oil, which is known as Cadet's fuming liquid, is chiefly composed of the arsenide of methyl $\left(\left.\begin{array}{r}CH^3\\ CH^3\end{array}\right\}As\right)^2$.

The pentachloride, terchloride, and oxychloride of phosphorus convert acetic acid into chloride of acetyl, volatile at 55°:



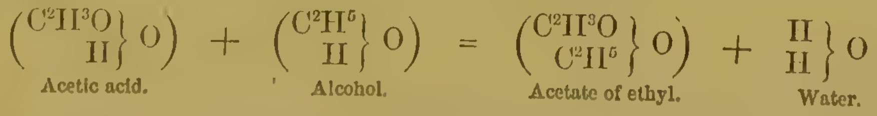
$$\underset{\text{Perchloride of phosphorus.}}{\left(PCl^5\right)} + \underset{\text{Acetic acid.}}{4\left(\left.\begin{array}{r}C^2H^3O\\ H\end{array}\right\}O\right)} = \underset{\text{Chloride of acetyl.}}{4\left(\left.\begin{array}{r}C^2H^3O\\ Cl\end{array}\right\}\right)} + \underset{\text{Hydrochloric acid.}}{\left.\begin{array}{r}H\\ Cl\end{array}\right\}} + \underset{\text{Phosphoric acid.}}{\left(PO'''\left\{\begin{array}{l}OH\\ OH\\ OH\end{array}\right.\right)}$$

Chloride of acetyl, distilled with acetate of potassium, is transformed into anhydrous acetic acid volatile at 137°·5:



$$\underset{\text{Chloride of acetyl.}}{\left(\left.\begin{array}{r}C^2H^3O\\ Cl\end{array}\right\}\right)} + \underset{\text{Potassic acetate.}}{\left(\left.\begin{array}{r}C^2H^3O\\ K\end{array}\right\}O\right)} = \underset{\text{Chloride of potassium.}}{\left.\begin{array}{r}K\\ Cl\end{array}\right\}} + \underset{\text{Acetic anhydride.}}{\left(\left.\begin{array}{r}C^2H^3O\\ C^2H^3O\end{array}\right\}O\right)}$$

When acetic acid is heated with the different alcohols in hermetically-sealed tubes it etherifies them; acetate of ethyl may be obtained in this manner:



$$\underset{\text{Acetic acid.}}{\left(\left.\begin{array}{r}C^2H^3O\\ H\end{array}\right\}O\right)} + \underset{\text{Alcohol.}}{\left(\left.\begin{array}{r}C^2H^5\\ H\end{array}\right\}O\right)} = \underset{\text{Acetate of ethyl.}}{\left(\left.\begin{array}{r}C^2H^3O\\ C^2H^5\end{array}\right\}O\right)} + \underset{\text{Water.}}{\left.\begin{array}{r}H\\ H\end{array}\right\}O}$$

The acetate of ethyl has an ethereal odour; it is slightly soluble in water. Bromine splits it up, forming bromacetic acid and bromide of thyl (*Crafts*):

$$\underset{\text{Acetate of ethyl.}}{\left(\left.\begin{matrix}C^2H^3O\\C^2H^5\end{matrix}\right\}O\right)} + \underset{\text{Bromine.}}{\left.\begin{matrix}Br\\Br\end{matrix}\right\}} = \underset{\text{Bromacetic acid.}}{\left(\left.\begin{matrix}C^2H^2BrO\\H\end{matrix}\right\}O\right)} + \underset{\text{Bromide of ethyl.}}{\left(\left.\begin{matrix}C^2H^5\\Br\end{matrix}\right\}\right)}$$

Acted upon by sodium, this ether exchanges one or two atoms of hydrogen for the metal. The products thus obtained enter into double decomposition with the iodides of ethyl and methyl, and give homologues of acetate of ethyl (Frankland):

$$\underset{\text{Acetate of ethyl.}}{\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H^3\\ \hline O\\OC^2H^5\end{array}\right.\right)} + \underset{\text{Sodium.}}{\left.\begin{matrix}Na\\Na\end{matrix}\right\}} = \underset{\text{Disodacetic ether.}}{\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}Na^2\\H\\ \hline O\\OC^2H^5\end{array}\right.\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}}$$

$$\underset{\text{Disodacetic ether.}}{\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}Na^2\\H\\ \hline O\\OC^2H^5\end{array}\right.\right)} + \underset{\text{Iodide of methyl.}}{2\left(\left.\begin{matrix}CH^3\\I\end{matrix}\right\}\right)} = \underset{\text{Iodide of sodium.}}{2\left(\left.\begin{matrix}Na\\I\end{matrix}\right\}\right)} + \underset{\text{Butyrate (dimethacetate) of ethyl.}}{\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}CH^3\\CH^3\\H\\ \hline O\\OC^2H^5\end{array}\right.\right)}$$

Acetic is a powerful acid, forming well-defined salts, resulting with monatomic metals from the substitution of an atom of metal for an atom of hydrogen. Several of these salts combine with a molecule of free acetic acid and form what are called binacetates:

$$\left(\left.\begin{matrix}C^2H^3O\\M'\end{matrix}\right\}O,\ \left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O\right).$$

In these compounds, acetic acid must be considered as acting the same part as the water of crystallization in salts.

The soluble acetates assume a deep-red colour when a little ferric chloride is added to their solution. This coloration is owing to the formation of ferric acetate, and disappears under the influence of agents which reduce the ferric to the state of ferrous acetate.

When heated with an excess of alkali, the acetates furnish marsh gas.

Distilled with dilute sulphuric acid, they give acetic acid, which may be recognized by its forming, when litharge is digested in it, a sub-salt of lead, which colours litmus paper blue.

**Butyric Acid** $\left(\left.\begin{matrix}C^4H^7O\\H\end{matrix}\right\}O\right)$.—PREPARATION.—1st. Butyric acid is found ready formed in the stalks and fruit of certain vegetables, such as the carob tree and tamarind, from which it may be extracted by distilling them with dilute sulphuric acid. It cannot however be obtained in large quantities by this process.

2nd. There exists in butter a neutral fatty body, glyceric tributyrate, which is resolved into an alkaline butyrate and glycerine when saponified with potash or soda:

$$\underset{\text{Glyceric tributyrate.}}{\left(\left.\begin{matrix}C^3H^{5'''}\\(C^4H^7O)^3\end{matrix}\right\}O^3\right)} + \underset{\text{Potassic hydrate.}}{3\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic butyrate.}}{3\left(\left.\begin{matrix}C^4H^7O\\K\end{matrix}\right\}O\right)} + \underset{\text{Glycerine.}}{\left(\left.\begin{matrix}C^3H^{5'''}\\H^3\end{matrix}\right\}O^3\right)}$$

It is from this compound that Chevreul first extracted it. But the butyrin is here mixed with a number of other neutral fatty bodies which are separated with difficulty, and many of which furnish volatile acids, homologues of butyric acid (caproic, caprylic, and capric acids), by distillation. Butyric acid prepared from butter is therefore very difficult to purify, and as moreover butter only yields the acid in small quantity, this process is not now employed.

3rd. Butyric acid is produced in a particular fermentation of the different kinds of sugars, starch, and other analogous substances. When these are left with casein or its congeners at a temperature of about 30° a mycoderm is first developed which acts as a ferment, and transforms them into lactic acid; then an infusorial animalcula, also acting as a ferment, is in its turn developed, and under its influence the lactic acid is converted into butyric acid, carbonic anhydride, and hydrogen.

The following equation shows the transformation:

$$\underset{\text{Lactic acid.}}{2(C^3H^6O^3)} = \underset{\text{Butyric acid.}}{(C^4H^8O^2)} + \underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{2(CO^2)} + \underset{\text{Hydrogen.}}{2H^2}$$

However, as a vital action, not a simple chemical reaction, is here in question, it is most probable that the phenomena are more complicated, and that this equation is only apparently correct.

The following is the method employed to prepare butyric acid by means of fermentation.

Three kilogrammes of cane sugar and fifteen grammes of tartaric acid are dissolved in fifteen kilogrammes of boiling water and left for several days; then sixty grammes of old decayed cheese, in four kilogrammes of curdled skim milk, along with half a kilogramme of washed chalk, are added to the mixture, which is left at a temperature of 30° or 35° and stirred several times a day; at the end of about ten days it has become a thick milky substance—lactate of calcium. After some days the mass again becomes more fluid and gas bubbles begin to be developed. When all gaseous disengagement has ceased, which will be after five or six weeks, the fermentation is completed. Then a solution of four kilogrammes of crystallized carbonate of sodium is added to the mixture, which is filtered through a linen cloth to separate the carbonate of calcium, which is well washed.

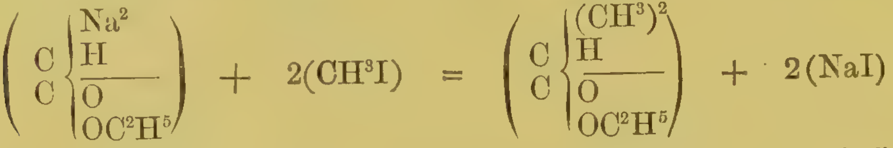
The filtered liquid is boiled down to five kilogrammes, then $2^{\text{kilo}}$ $750^{\text{gr}}$ of sulphuric acid are added to it; the greater part of the butyric acid is then separated in the form of an oil which floats on the surface of the liquid, and is decanted off. The aqueous liquid is then distilled. The product of the distillation, saturated by sodic carbonate, suitably evaporated, and acted upon by sulphuric acid, gives a fresh quantity of butyric acid which is added to the first.

The butyric acid thus obtained is distilled, after sixty grammes of sulphuric acid have been added for each kilogramme. This acid transforms the neutral sodic sulphate with which the butyric acid is mixed into acid sulphate, as it would interfere with the distillation. The first portions which come over, and which are hydrated, are set aside. The receiver is changed when the temperature has attained 164°. That which then passes over is pure butyric acid.

Schubert proposes to replace the cheese by meat, and the sugar by starch in this operation (1 part of meat to 4 of starch); the fermentation would then, according to him, be completed in five or six days. According to Wicklès, this process is very economical and has the advantage of being successful on a small scale.

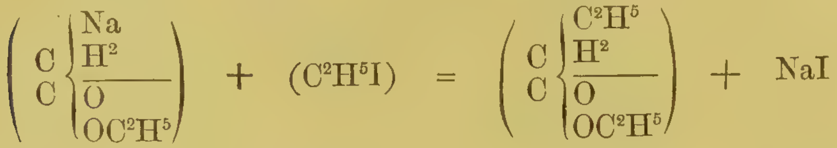
4th. Butyric acid may also be prepared by the oxidation of butylic alcohol, which is extracted by fractional distillation from the same residues used for the extraction of amylic alcohol. But as these residues only contain very little butylic alcohol, and as much time is required to separate this alcohol in a pure state, this method of procuring butyric acid is never employed.

5th. When iodide of methyl or of ethyl is made to act on the sodic derivatives of acetate of ethyl, bodies are obtained which have the same composition as the butyrate of ethyl, and which consequently by saponification would give acids of the same composition as butyric acid (Frankland and Duppa).



$$\left(\begin{array}{l}C\\C\end{array}\left\{\begin{array}{l}Na^2\\H\\\hline O\\OC^2H^5\end{array}\right.\right)+2(CH^3I)=\left(\begin{array}{l}C\\C\end{array}\left\{\begin{array}{l}(CH^3)^2\\H\\\hline O\\OC^2H^5\end{array}\right.\right)+2(NaI)$$

Disodacetic ether. Iodide of methyl. Dimethacetate of ethyl. Iodide of sodium.



$$\left(\begin{array}{l}C\\C\end{array}\left\{\begin{array}{l}Na\\H^2\\\hline O\\OC^2H^5\end{array}\right.\right)+(C^2H^5I)=\left(\begin{array}{l}C\\C\end{array}\left\{\begin{array}{l}C^2H^5\\H^2\\\hline O\\OC^2H^5\end{array}\right.\right)+NaI$$

Monosodacetic ether. Iodide of ethyl. Ethacetate of ethyl. Iodide of sodium.

Would the dimethacetate and the ethacetate of ethyl give two acids identical with the butyric acid of fermentation, or are these three acids isomers? This is not yet known. It is, however, probable that ethacetic acid is identical with the butyric acid of fermentation, and isomeric with dimethacetic acid.

Properties.—Pure butyric acid is a colourless and very unstable liquid; its odour is something between that of rancid butter and acetic acid, and it has an acrid burning taste.

The density of butyric acid at its maximum of concentration is 0·9886 at 0°, to 0·9739 at 15°, and 0·9675 at 25°; the density of a mixture of two parts of this acid and one part of water is 1·00287.

Butyric acid is soluble in all proportions in water, alcohol, or wood-spirit. It boils at 164°; its vapour density has been found to be 3·7 at the temperature of 261°. As in the case of acetic acid, this number only becomes constant at a temperature considerably above its boiling point. Butyric acid remains fluid at – 20°, but it crystallizes in large plates in a mixture of solid carbonic anhydride and ether. It corrodes the skin. Its vapour burns with a blue flame.

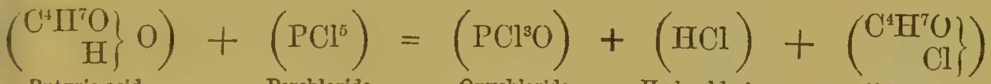
Butyric acid is not altered by sulphuric acid at the ordinary temperature, and is only partially decomposed when their mixture is heated. Cold nitric acid does not attack it, but when boiled with it for some time transforms it into succinic acid:

$$\underset{\text{Butyric acid.}}{2(C^4H^8O^2)} + \underset{\text{Oxygen.}}{3O^2} = \underset{\text{Water.}}{2(H^2O)} + \underset{\text{Succinic acid.}}{2(C^4H^6O^4)}$$

In sunlight dry chlorine converts butyric acid first into bichloro-butyric acid and then into quadrichloro-butyric acid.

Bromine does not act on it in the cold, but if a mixture of these two substances be placed in a hermetically-sealed tube and heated to between 150° and 200°, hydrobromic acid and, according to the quantity of bromine, monobromo- or bibromo-butyric acid are formed. The latter is crystallizable. In performing this experiment it often happens that carbon is deposited, a portion of the acid being entirely decomposed and yielding its oxygen to another part, which is converted into succinic acid.

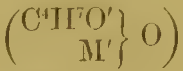
The perchloride of phosphorus transforms butyric acid into chloride of butyryl:



$$\underset{\text{Butyric acid.}}{\left(\left.\begin{matrix}C^4H^7O\\H\end{matrix}\right\}O\right)} + \underset{\substack{\text{Perchloride}\\\text{of phosphorus.}}}{\left(PCl^5\right)} = \underset{\substack{\text{Oxychloride}\\\text{of phosphorus.}}}{\left(PCl^3O\right)} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{\left(HCl\right)} + \underset{\substack{\text{Chloride of}\\\text{butyryl.}}}{\left(\left.\begin{matrix}C^4H^7O\\Cl\end{matrix}\right\}\right)}$$

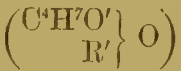
This chloride boils at 95°. It is decomposed by water, butyric and hydrochloric acids being formed; when distilled with dry sodic butyrate, it furnishes chloride of sodium and butyric anhydride, which is volatile at 190°.

Butyric acid is monobasic and monatomic, and exchanges an atom of hydrogen for an atom of a metal, or for a radicle of a monatomic alcohol, thus forming neutral salts or ethers:



$$\left(\left.\begin{matrix}C^4H^7O'\\M'\end{matrix}\right\}O\right)$$

Neutral butyrate.



$$\left(\left.\begin{matrix}C^4H^7O'\\R'\end{matrix}\right\}O\right)$$

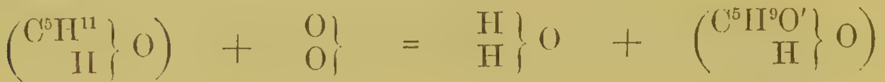
Neutral butyric ether.

When dry, butyrates have no odour, but when moist they smell like butter. They are generally soluble in water and crystallizable; when thrown upon water they often present rapid gyratory motions.

When butyrate of calcium is submitted to dry distillation butyrone

$(C^7H^{14}O) = \left(\left.\begin{matrix}C^4H^7O\\C^3H^7\end{matrix}\right\}\right)$ passes over; in this case lower acetones of the same series are also produced.

**Valeric Acid** $\left(\left.\begin{matrix}C^5H^9O'\\H\end{matrix}\right\}O\right)$.—PREPARATION.—This acid was first extracted from the oil of the porpoise, which contains its elements; later it was procured from valerian root, but now it is always prepared by oxidizing amylic alcohol, whence it is derived by the substitution of O for $H^2$:



$$\left(\left.\begin{matrix}C^5H^{11}\\H\end{matrix}\right\}O\right) + \left.\begin{matrix}O\\O\end{matrix}\right\} = \left.\begin{matrix}H\\H\end{matrix}\right\}O + \left(\left.\begin{matrix}C^5H^9O'\\H\end{matrix}\right\}O\right)$$

Amylic alcohol. Oxygen. Water. Valeric acid.

The operation is conducted in the following manner:

Amylic alcohol is dissolved in concentrated sulphuric acid; this solution is gradually poured into an aqueous solution of bichromate of potassium, and distilled when the reaction has ceased. An aqueous solution of valeric acid, covered by an oily layer of valeric aldehyd, passes over. The aldehyd is decanted, and the acid liquid is saturated by an alkaline carbonate and evaporated to dryness. The alkaline valerate is then distilled with dilute sulphuric acid, and the product is submitted to fractional distillation, by means of which it is freed from the water it contains.

A mixture of one part of amylic alcohol and ten parts of potash-lime may be heated first to 175°, then to 200° for 10 or 12 hours, until all gaseous disengagement ceases. The mixture must be protected from the air while cooling or it will take fire. It is then distilled with dilute sulphuric acid. The product is saturated with sodic carbonate and evaporated to dryness, by which it is freed from any oily matters it may contain. After this it is distilled with sulphuric acid, and separated from the water by additional rectifications.

PROPERTIES.—Valeric acid is an unstable, colourless, limpid liquid, of an acrid, pungent taste, and a powerful odour resembling that of valerian root; it boils without decomposition at 175°, and remains fluid at $-15°$. Its density is 0·937 at 16°·5; its vapour density is 3·67. It produces a white mark on the tongue.

The vapour of valeric acid burns with a sooty flame. When a valerate dissolved in water is decomposed by means of a mineral acid, valeric acid is separated in the form of an oily hydrate $C^5H^{10}O^2 + aq.$, which boils at a lower temperature than the normal acid, losing its water by heat, and the density of which (0·950) is greater than that of the dry acid.

Valeric acid mixes with alcohol and ether in all proportions; acetic acid of the density 1·07 also dissolves it largely, but water at 12° only dissolves a thirtieth part of its weight; therefore an alcoholic solution of valeric acid becomes cloudy on the addition of a small quantity of water, but becomes clear again when a considerable quantity is added.

Camphor and some of the resins are dissolved by valeric acid; sulphur is entirely insoluble in it.

Valeric acid is charred by hot sulphuric acid, disengaging sulphurous anhydride. Concentrated nitric acid converts it into nitro-valeric acid:

$$\underset{\text{Valeric acid.}}{(C^5H^{10}O^2)} + \underset{\text{Nitric acid.}}{(NHO^3)} = \underset{\text{Water.}}{(H^2O)} + \underset{\text{Nitro-valeric acid.}}{(C^5H^9(NO^2)O^2)}$$

The vapour of valeric acid, transmitted through a red-hot tube full of fragments of pumice-stone, is resolved into several gases, among which may be distinguished carbonic anhydride, oxide of carbon, ethylene, propylene, butylene, and perhaps other hydrocarbides of the series $C^nH^{2n}$. Propylene ($C^3H^6$) appears to be the most abundant of these hydrocarbides.

When distilled with an excess of baryta, valeric acid also gives gaseous products, among which are found hydrocarbides of the ethylene series ($C^nH^{2n}$), free hydrogen, and perhaps marsh gas.

Chlorine transforms valeric acid into products of substitution. Bromine does not attack it in the cold, but at 100° it transforms it into bromo-valeric acid.

Valeric acid is a bad conductor of electricity, but when potassic valerate in aqueous solution, is submitted to the influence of the electric current, hydrogen, carbonic gas, and butylene ($C^4H^8$) are disengaged, and there is produced at the same time liquid dibutyl ($C^8H^{18}$) which floats on the surface of the mixed liquids.

Valeric acid forms defined salts arising from the substitution of a metal for the typical hydrogen the acid contains. These salts correspond to the general formula $\left(\left.\begin{matrix}C^5H^9O\\M'\end{matrix}\right\}O\right)$.

Under the influence of oxychloride of phosphorus, the valerate of potassium when quite dry is transformed into valeric anhydride, volatile at 215°.

$$\underset{\text{Oxychloride of phosphorus.}}{\left(PO'''\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right.\right)} + \underset{\text{Valerate of potassium.}}{6\left(\left.\begin{matrix}C^5H^9O\\K\end{matrix}\right\}O\right)} = \underset{\text{Phosphate of potassium.}}{\left(PO'''\left\{\begin{matrix}OK\\OK\\OK\end{matrix}\right.\right)} + \underset{\text{Chloride of potassium.}}{3\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)}$$

$$+ \underset{\text{Valeric anhydride.}}{3\left(\left.\begin{matrix}C^5H^9O\\C^5H^9O\end{matrix}\right\}O\right)}$$

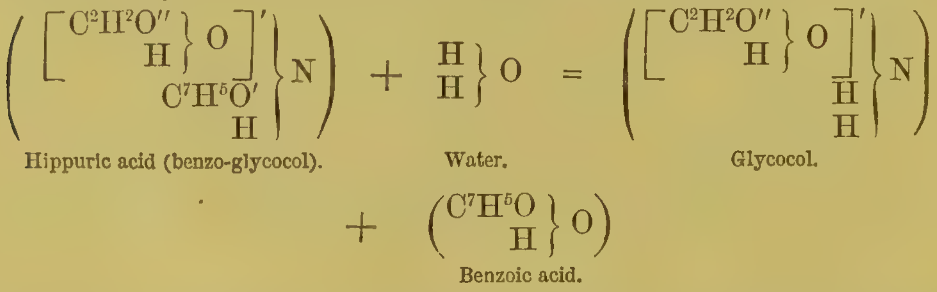
The valerates when dry are without odour, but when moist they have a strong smell of valeric acid. They possess the property of gyrating on the surface of water, and many of them, especially the alkaline valerates, have a sweet taste.

**Benzoic Acid** $\left(\left.\begin{matrix}C^7H^5O\\H\end{matrix}\right\}O\right)$.—Benzoic acid has long been known, and is obtained in a number of reactions.

Preparation.—1st. Benzoic acid is extracted from the resin of benzoin, in which it exists ready formed. To effect this, 500 grammes of the coarsely-powdered resin are placed in an iron vessel of from 10 to 12 inches in diameter and 1 to 2 inches in depth. The vessel is tightly covered with a sheet of bibulous paper, above which is fitted a cylinder of cardboard about the size of a man's hat, open at the lower part but closed at the top. The vessel is then heated in a sand-bath at a moderate temperature for three or four hours. The benzoic acid in vapour passes through the diaphragm of bibulous paper, and is crystallized in the cardboard cylinder, while the diaphragm retains the oily and empyreumatic products.

This process is far from giving all the benzoic acid contained in the benzoin. A better method consists in boiling the powdered resin for several hours with milk of lime, filtering and concentrating the liquid, and then precipitating by hydrochloric acid. The benzoic acid which is deposited should be purified by sublimation or by crystallization from boiling water.

2nd. Benzoic acid having of late years become an article of commerce, it is now manufactured from the urine of the herbivora, which contains hippuric acid. To effect this, the urine is boiled with hydrochloric acid, and allowed to cool, when benzoic acid is deposited in crystals, and has only to be purified by solution in boiling water and a second crystallization. The urines from which the benzoic acid is deposited hold glycocol (glycolamidic acid) ($C^2N^5HO^2$) in solution.



$$\left(\left.\begin{matrix}\left[\left.\begin{matrix}C^2H^2O''\\H\end{matrix}\right\}O\right]'\\C^7H^5O'\\H\end{matrix}\right\}N\right) + \left.\begin{matrix}H\\H\end{matrix}\right\}O = \left(\left.\begin{matrix}\left[\left.\begin{matrix}C^2H^2O''\\H\end{matrix}\right\}O\right]'\\H\\H\end{matrix}\right\}N\right) + \left(\left.\begin{matrix}C^7H^5O\\H\end{matrix}\right\}O\right)$$

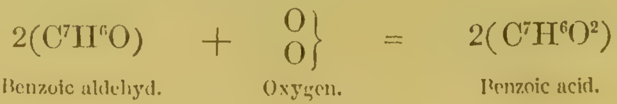
Hippuric acid (benzo-glycocol). Water. Glycocol. Benzoic acid.

3rd. MM. Lauth and Grimaux have found that considerable quantities of benzoic acid are obtained when monochlorinated toluene (chloride of benzyl) is oxidized by nitric acid.

The two first methods of preparation are the only ones used in manufactures, but that of MM. Lauth and Grimaux deserves to replace them.

Besides these processes, benzoic acid may also be obtained by the following methods.

4th. Benzoic aldehyd (essential oil of bitter almonds), extracted from bitter almonds by distilling them with water, oxidizes in the air and is thereby converted into benzoic acid:



$$2(C^7H^6O) + \left.\begin{matrix}O\\O\end{matrix}\right\} = 2(C^7H^6O^2)$$

Benzoic aldehyd. Oxygen. Benzoic acid.

5th. Trichlorinated toluene is transformed into benzoate and chloride of potassium when heated with a concentrated solution of potassic hydrate in alcohol (Naquet):

$$\underset{\text{Trichlorinated toluene.}}{\left(C^7H^5Cl^3\right)} + \underset{\text{Potassic hydrate.}}{4\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Benzoate of potassium.}}{\left(\left.\begin{matrix}C^7H^5O\\K\end{matrix}\right\}O\right)} + \underset{\text{Chloride of potassium.}}{3\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)}$$

$$+ \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

6th. Benzoic acid is formed when water acts on the chloride of benzoyl, and this latter is obtained by the reaction of benzine in vapour on the oxychloride of carbon (Harnitz-Harnitzky):

$$\underset{\text{Benzine.}}{\left(C^6H^6\right)} + \underset{\text{Oxychloride of carbon.}}{\left(CO''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)} = \underset{\text{Chloride of benzoyl.}}{\left(\left.\begin{matrix}C^6H^5(CO)\\Cl\end{matrix}\right\}\right)} + \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}}$$

$$\underset{\text{Chloride of benzoyl.}}{\left(\left.\begin{matrix}C^6H^5(CO)\\Cl\end{matrix}\right\}\right)} + \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O} = \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}} + \underset{\text{Benzoic acid.}}{\left(\left.\begin{matrix}C^7H^5O\\H\end{matrix}\right\}O\right)}$$

7th. Benzoic acid is produced in a number of reactions, as in the oxidation of cumene, ethyl-benzine, cinnamic aldehyd, cinnamic acid, cinnamene, casein, gelatine, etc., etc.*

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* Hofmann has just discovered a very elegant synthetical process, by means of which he has prepared benzoic acid and all its true homologues, as well as a new acid ($C^{11}H^8O^2$) which bears the same relation to naphthalin that benzoic acid does to benzine, that is to say, it is derived from naphthalin by the substitution of $\left(C\left\{\begin{matrix}O''\\OH\end{matrix}\right.\right)'$ for H. To effect this, Hofmann prepares the compound ammonias which are derived from the fundamental hydrocarbides, benzine, toluene, naphthalin, etc. (he uses the bases analogous to aniline, and not to benzylamine and its homologues), and then distils these bases with oxalic acid. One molecule of oxide of carbon is detached from this acid and unites with the typical hydrogen of the base, to form formyl (COH), and phenylic, cresylic, or naphthylic, etc., formamide is produced. The compound formamide thus obtained is deprived of $H^2O$ by distillation, and gives the cyanide of its phenic radicle. By boiling with an alcoholic solution of potash, these cyanides furnish the salts of the acid sought for. The following are the reactions just described:

1st. $$\underset{\text{Naphthylamine.}}{\left(\left.\begin{matrix}C^{10}H^7\\H\\H\end{matrix}\right\}N\right)} + \underset{\text{Oxalic acid.}}{\left(\left.\begin{matrix}C^2O^2\\H^2\end{matrix}\right\}O^2\right)} = \underset{\text{Naphthyl-formamide.}}{\left(\left.\begin{matrix}C^{10}H^7\\COH\\H\end{matrix}\right\}N\right)} + \underset{\text{Carbonic anhydride.}}{CO^2} + \underset{\text{Water.}}{H^2O}$$

2nd. $$\underset{\text{Naphthyl-formamide.}}{\left(\left.\begin{matrix}C^{10}H^7\\COH\\H\end{matrix}\right\}N\right)} = \underset{\text{Water.}}{H^2O} + \underset{\text{Cyanide of naphthyl.}}{(C^{10}H^7CN)}$$

Properties.—Benzoic acid crystallizes in plates or in transparent flexible needles; it has an agreeable odour resembling that of benzoin, and an acrid acid taste. It melts at 120°, sublimes at 145°, and boils without decomposition at 239°; its vapours are acrid and excite coughing. It dissolves in twice its weight of boiling water, but requires two hundred times its weight of cold water for solution: alcohol and ether readily dissolve it.

Concentrated sulphuric dissolves benzoic acid, but water precipitates the latter from this solution. Nordhausen sulphuric acid, and especially sulphuric anhydride, convert benzoic into sulphobenzoic acid. As this latter forms a salt of barium which is soluble in water, it may be readily separated from any excess of sulphuric anhydride. To effect this, it has only to be dissolved in water, the solution precipitated by baryta, and a current of carbonic gas transmitted through it to eliminate the excess of hydrate, and then filtered and left to evaporate, when the sulphobenzoate of barium crystallizes:

$$\underset{\text{Benzoic acid.}}{\left(\left.\begin{matrix}C^7H^5O\\H\end{matrix}\right\}O\right)} + \underset{\text{Sulphuric anhydride.}}{\left(SO^{2\prime\prime}O\right)}$$

$$= \underbrace{\left(\left.\begin{matrix}C^7H^4(SO^2OH)'\\H\end{matrix}\right\}O\right) = \left((C^7H^4SO^2)''\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)}_{\text{Sulphobenzoic acid.}}$$

Concentrated nitric acid transforms benzoic into nitrobenzoic acid, and a mixture of sulphuric and nitric acids converts it into binitrobenzoic acid:

$$\underset{\text{Benzoic acid.}}{\left(\left.\begin{matrix}C^7H^5O\\H\end{matrix}\right\}O\right)} + \underset{\text{Nitric acid.}}{\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)} = \underset{\text{Nitrobenzoic acid.}}{\left(\left.\begin{matrix}C^7H^4(NO^2)O\\H\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O}$$

$$\underset{\text{Benzoic acid.}}{\left(\left.\begin{matrix}C^7H^5O\\H\end{matrix}\right\}O\right)} + \underset{\text{Nitric acid.}}{2\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)} = \underset{\text{Binitrobenzoic acid.}}{\left(\left.\begin{matrix}C^7H^3(NO^2)^2O\\H\end{matrix}\right\}O\right)}$$

$$+ \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

Nitrobenzoic acid gives oxybenzamic, improperly called benzamic acid, when submitted to the influence of reducing agents:

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$$\text{3rd.}\quad \underset{\text{Cyanide of naphthyl.}}{(C^{10}H^7CN)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Ammonia.}}{\left(N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.\right)}$$

$$+ \underset{\text{Salt of new acid.}}{\left(C^{10}H^7C\left\{\begin{matrix}O''\\OK\end{matrix}\right.\right)}$$

$$\begin{array}{ccccc}
\left(\left.\begin{matrix}C^7H^4(NO^2)O\\ H\end{matrix}\right\}O\right) & + & 3\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}\right) & = & \left.\begin{matrix}\left(\left.\begin{matrix}C^7H^4O''\\ H\end{matrix}\right\}O\right)'\\ H\\ H\end{matrix}\right\}N\\
\text{Benzamic acid.} & & \text{Hydrogen.} & & \text{Oxybenzamic acid.}
\end{array}$$

$$\begin{array}{c} +\; 2\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)\\ \text{Water.}\end{array}$$

In sunlight, chlorine appears to give substitution products with benzoic acid. The monochlorinated derivative is moreover easily obtained by heating benzoic acid with perchloride of antimony.

Bromine does not act on benzoic acid in the cold, but it converts benzoate of silver into bromobenzoic acid. This latter gives oxybenzamic acid by the action of ammonia (Alexeïef):

$$\begin{array}{ccccccc}
(C^7H^5AgO^2) & + & Br^2 & = & (AgBr) & + & (C^7H^5BrO^2)\\
\text{Benzoate of silver.} & & \text{Bromine.} & & \text{Bromide of silver.} & & \text{Bromobenzoic acid.}
\end{array}$$

$$\begin{array}{ccccccc}
(C^7H^5BrO^2) & + & 2(NH^3) & = & (C^7H^7NO^2) & + & (NH^4Br)\\
\text{Bromobenzoic acid.} & & \text{Ammonia.} & & \text{Oxybenzamic acid.} & & \text{Bromide of ammonium.}
\end{array}$$

Submitted to the influence of nascent hydrogen, benzoic acid is reduced, part into benzoic aldehyd (Kolbe) or benzylic alcohol (Friedel), and part fixes H², giving a new acid, the hydrobenzoic:

$$\begin{array}{ccccccc}
\left(\left.\begin{matrix}C^7H^5O\\ H\end{matrix}\right\}O\right) & + & \left.\begin{matrix}H\\ H\end{matrix}\right\} & = & \left.\begin{matrix}H\\ H\end{matrix}\right\}O & + & \left(\left.\begin{matrix}C^7H^5O\\ H\end{matrix}\right\}\right)\\
\text{Benzoic acid.} & & \text{Hydrogen.} & & \text{Water.} & & \text{Benzoic aldehyd.}
\end{array}$$

$$\begin{array}{ccccccc}
\left(\left.\begin{matrix}C^7H^5O\\ H\end{matrix}\right\}O\right) & + & 2\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}\right) & = & \left.\begin{matrix}H\\ H\end{matrix}\right\}O & + & \left(\left.\begin{matrix}C^7H^7\\ H\end{matrix}\right\}O\right)\\
\text{Benzoic acid.} & & \text{Hydrogen.} & & \text{Water.} & & \text{Benzylic alcohol.}
\end{array}$$

$$\begin{array}{ccccc}
\left(\left.\begin{matrix}C^7H^5O\\ H\end{matrix}\right\}O\right) & + & \left.\begin{matrix}H\\ H\end{matrix}\right\} & = & \left(\left.\begin{matrix}C^7H^7O\\ H\end{matrix}\right\}O\right)\\
\text{Benzoic acid.} & & \text{Hydrogen.} & & \text{Hydrobenzoic acid.}
\end{array}$$

Distilled with an excess of lime or baryta, benzoic acid is split up into carbonic anhydride and benzine (C⁶H⁶); the same division takes place when vapours of the acid are transmitted through a red-hot tube, or when one part of the acid is distilled with five or six parts of finely-powdered pumice-stone:

$$\begin{array}{ccccc}
(C^7H^6O^2) & = & (CO^2) & + & (C^6H^6)\\
\text{Benzoic acid.} & & \text{Carbonic anhydride.} & & \text{Benzine.}
\end{array}$$

When benzoic acid is treated with perchloride of phosphorus, chloride of benzoyl is produced:

$$\begin{array}{ccccccccc}
\left(\left.\begin{matrix}C^7H^5O\\ H\end{matrix}\right\}O\right) & + & (PCl^5) & = & (PCl^3O) & + & \left.\begin{matrix}H\\ Cl\end{matrix}\right\} & + & \left(\left.\begin{matrix}C^7H^5O\\ Cl\end{matrix}\right\}\right)\\
\text{Benzoic acid.} & & \text{Perchloride of phosphorus.} & & \text{Oxychloride of phosphorus.} & & \text{Hydrochloric acid.} & & \text{Chloride of benzoyl.}
\end{array}$$

This chloride boils at 196°. When distilled with dry benzoate of sodium, it gives benzoic anhydride, which is a crystallizable body, fusible at 42°, and volatile without decomposition at 310°:

$$\underset{\text{Chloride of benzoyl.}}{\left(\left.\begin{matrix}C^7H^5O\\ Cl\end{matrix}\right\}\right)} + \underset{\text{Benzoate of potassium.}}{\left(\left.\begin{matrix}C^7H^5O\\ K\end{matrix}\right\}O\right)} = \underset{\text{Chloride of potassium.}}{\left.\begin{matrix}K\\ Cl\end{matrix}\right\}} + \underset{\text{Benzoic anhydride.}}{\left(\left.\begin{matrix}C^7H^5O\\ C^7H^5O\end{matrix}\right\}O\right)}$$

Benzoic acid, on reacting with bases, exchanges its typical hydrogen for a metal, forming salts which correspond to the general formula $\left(\left.\begin{matrix}C^7H^5O\\ M'\end{matrix}\right\}O\right)$.

Most of the benzoates are soluble in water. Benzoic acid is precipitated from their solutions by the soluble mineral and organic acids. Benzoate of calcium submitted to dry distillation yields benzophenone ($C^{13}H^{10}O$), benzine ($C^6H^6$), diphenyl ($C^{12}H^{10}$), and a hydrocarbide isomeric with naphthalin ($C^{10}H^8$).

Benzoic acid readily etherifies the alcohols under the action of a current of hydrochloric acid gas.

## *Appendix to Benzoic Acid.*

**Hippuric Acid.**—Hippuric acid is found combined with soda or ammonia in the urine of the herbivora; it is also found in human urine, but in much smaller proportion. The quantity is said to be increased in some diseases, such as diabetes and Saint Vitus' dance; it is also increased by the ingestion of certain substances such as benzoic acid, benzoic ether, benzoic aldehyd and cinnamic acid. It cannot be doubted in this case that the hippuric acid is owing to the benzoic acid taken into the system, for if one of its homologues be eaten instead of it, toluic acid for instance, the urine contains a homologue of hippuric acid.

When horses have been worked hard, their urine contains benzoic instead of hippuric acid.

Preparation.—1st. Hippuric acid may be obtained by the reaction of chloride of benzoyl on argentic or zinc glycocol (Dessaignes):

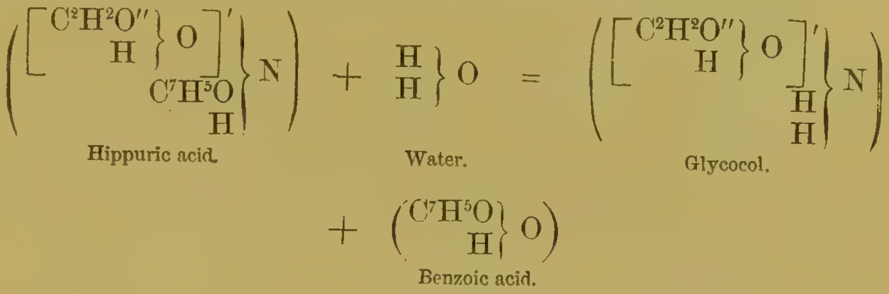
$$\underset{\text{Argentine glycocol.}}{(C^2H^4AgNO^2)} + \underset{\text{Chloride of benzoyl.}}{(C^7H^5OCl)} = \underset{\text{Chloride of silver.}}{(AgCl)} + \underset{\text{Hippuric acid.}}{(C^9H^9NO^3)}$$

2nd. But it is generally procured from the urine of the cow. According to Gregory, the best method of effecting this consists in adding milk of lime to the fresh urine, boiling for a few minutes, filtering, and evaporating to one-tenth of the original quantity. The liquid thus concentrated is supersaturated with hydrochloric acid: on cooling, it furnishes abundant crystals of impure hippuric acid, which must be purified by being transformed into a salt of calcium.

Properties.—Hippuric acid crystallizes in large brilliant crystals belonging to the rhombic system, of a density of 1·308. It has a bitter taste and requires 600 parts of water at 0° for its solution, but it is soluble in a much smaller proportion of boiling water. Its aqueous solution reddens litmus slightly. Acohol readily dissolves it, but in ether it is nearly insoluble, as it also is in water acidulated with hydrochloric acid.

It melts at a gentle heat, boils at 240° with decomposition, forming benzoic acid, cyanide of phenyl, charcoal, and a product which has a strong smell of hydrocyanic acid.

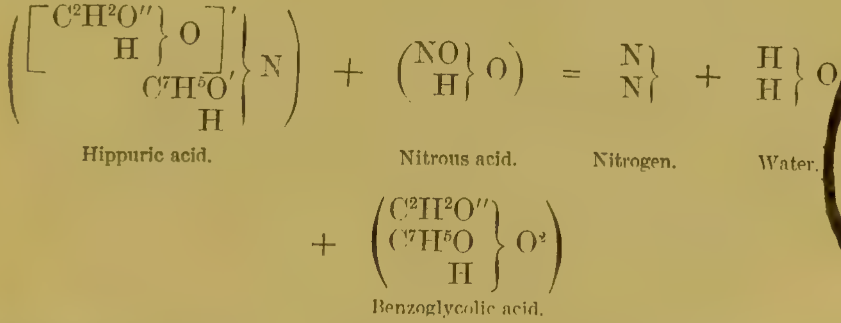
Treated with boiling dilute mineral acids, hippuric acid fixes water and is converted into glycocol and benzoic acid :



$$\underset{\text{Hippuric acid.}}{\left(\left.\begin{matrix}\left[\left.\begin{matrix}C^2H^2O''\\H\end{matrix}\right\}O\right]'\\C^7H^5O\\H\end{matrix}\right\}N\right)} + \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O} = \underset{\text{Glycocol.}}{\left(\left.\begin{matrix}\left[\left.\begin{matrix}C^2H^2O''\\H\end{matrix}\right\}O\right]'\\H\\H\end{matrix}\right\}N\right)} + \underset{\text{Benzoic acid.}}{\left(\left.\begin{matrix}C^7H^5O\\H\end{matrix}\right\}O\right)}$$

Boiling alkaline solutions give rise to the same division, the benzoic acid then remaining in the state of a benzoate.

Nitrous acid converts hippuric into benzoglycolic acid, water and free nitrogen :



$$\underset{\text{Hippuric acid.}}{\left(\left.\begin{matrix}\left[\left.\begin{matrix}C^2H^2O''\\H\end{matrix}\right\}O\right]'\\C^7H^5O'\\H\end{matrix}\right\}N\right)} + \underset{\text{Nitrous acid.}}{\left(\left.\begin{matrix}NO\\H\end{matrix}\right\}O\right)} = \underset{\text{Nitrogen.}}{\left.\begin{matrix}N\\N\end{matrix}\right\}} + \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O} + \underset{\text{Benzoglycolic acid.}}{\left(\left.\begin{matrix}C^2H^2O''\\C^7H^5O\\H\end{matrix}\right\}O^2\right)}$$

Boiled with oxidizing agents, such as peroxide of lead ($PbO^2$), hippuric acid gives water, carbonic anhydride and benzamide (Fehling) :

$$\underset{\text{Hippuric acid.}}{2(C^9H^9NO^3)} + \underset{\text{Oxygen.}}{3O^2} = \underset{\text{Water.}}{2(H^2O)} + \underset{\text{Carbonic anhydride.}}{4(CO^2)} + \underset{\text{Benzamide.}}{2(C^7H^7NO)}$$

An aqueous solution of sodic phosphate dissolves hippuric acid so largely that the solution loses its alkaline reaction and becomes acid. This explains the acidity of the fresh urine of man and animals.

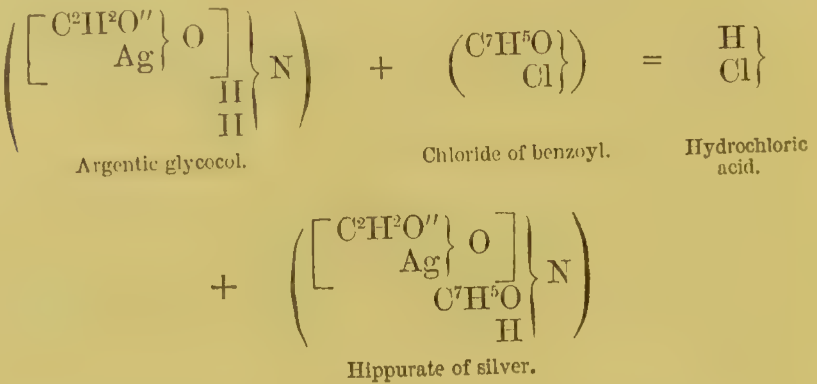
Hippuric acid exchanges an atom of hydrogen for monatomic metals, forming salts the general formula of which is ($C^9H^8M'NO^3$), and which, when distilled with an excess of lime, give benzine and ammonia.

LEEDS SCHOOL OF

Constitution of Hippuric Acid.—Hippuric acid is a secondary amide derived from a molecule of ammonia, one atom of the hydrogen of which is replaced by the monatomic residue of glycolic acid $\left(\left.\begin{matrix}C^2H^2O\\H\end{matrix}\right\}O\right)$ and the other by benzoyl ($C^7H^5O$): all its reactions are well explained by this hypothesis.

It is the same with its synthetical production by means of the chloride of benzoyl and the argentic salt of glycocol. But, as the atom of hydrogen which in this salt is replaced by silver is not the same as that which, in hippuric acid, is replaced by benzoyl, it must be supposed that the reaction is accomplished in two stages. In the first, the chloride of benzoyl in reacting on argentic glycocol would produce hippurate of silver and hydrochloric acid, and in the second this hydrochloric acid acting on the hippurate of silver would form hippuric acid and chloride of silver:

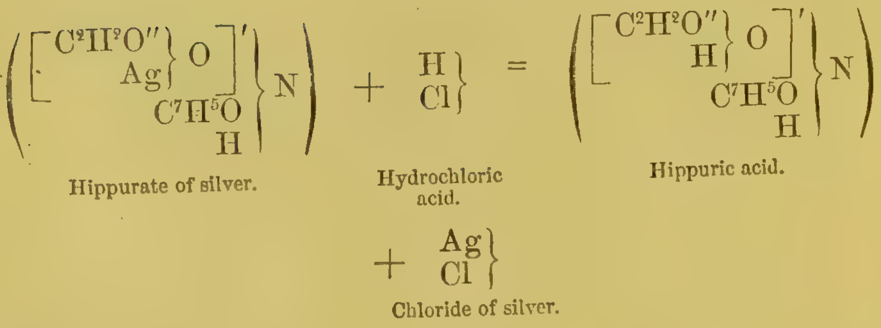
1st.



$$\left(\left.\begin{matrix}\left[\left.\begin{matrix}C^2H^2O''\\Ag\end{matrix}\right\}O\right]\\H\\H\end{matrix}\right\}N\right) + \left(\left.\begin{matrix}C^7H^5O\\Cl\end{matrix}\right\}\right) = \left.\begin{matrix}H\\Cl\end{matrix}\right\} + \left(\left.\begin{matrix}\left[\left.\begin{matrix}C^2H^2O''\\Ag\end{matrix}\right\}O\right]\\C^7H^5O\\H\end{matrix}\right\}N\right)$$

Argentic glycocol. Chloride of benzoyl. Hydrochloric acid. Hippurate of silver.

2nd.



$$\left(\left.\begin{matrix}\left[\left.\begin{matrix}C^2H^2O''\\Ag\end{matrix}\right\}O\right]'\\C^7H^5O\\H\end{matrix}\right\}N\right) + \left.\begin{matrix}H\\Cl\end{matrix}\right\} = \left(\left.\begin{matrix}\left[\left.\begin{matrix}C^2H^2O''\\H\end{matrix}\right\}O\right]'\\C^7H^5O\\H\end{matrix}\right\}N\right) + \left.\begin{matrix}Ag\\Cl\end{matrix}\right\}$$

Hippurate of silver. Hydrochloric acid. Hippuric acid. Chloride of silver.

## BIATOMIC ACIDS.

These acids are derived from biatomic alcohols by the substitution of $O$ for $H^2$, when they contain three atoms of oxygen and are only monobasic; or by the substitution of $O^2$ for $H^4$, when they are bibasic and contain four atoms of oxygen.

As to each series of hydrocarbides there corresponds a series of monatomic alcohols and a series of monatomic acids, so also to each of these same series of hydrocarbides there corresponds a series of glycols, a series of biatomic and monobasic acids, and a series of biatomic and bibasic acids.

HYDROCARBIDES.

$C^nH^{2n+2}$, $C^nH^{2n}$, $C^nH^{2n-2}$, $C^nH^{2n-4}$, $C^nH^{2n-6}$, $C^nH^{2n-8}$.

GLYCOLS.

$C^nH^{2n+2}O^2$, $C^nH^{2n}O^2$, $C^nH^{2n-2}O^2$, $C^nH^{2n-4}O^2$, $C^nH^{2n-6}O^2$, $C^nH^{2n-8}O^2$.

BIATOMIC AND MONOBASIC ACIDS.

$C^nH^{2n}O^3$, $C^nH^{2n-2}O^3$, $C^nH^{2n-4}O^3$, $C^nH^{2n-6}O^3$, $C^nH^{2n-8}O^3$, $C^nH^{2n-10}O^3$.

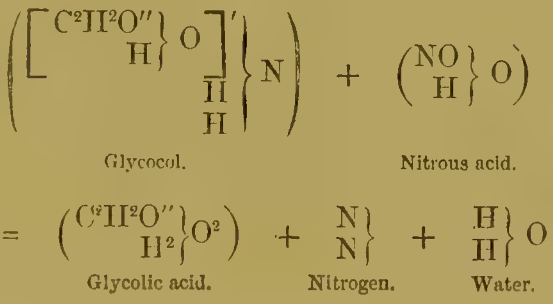
BIATOMIC AND BIBASIC ACIDS.

$C^nH^{2n-2}O^4$, $C^nH^{2n-4}O^4$, $C^nH^{2n-6}O^4$, $C^nH^{2n-8}O^4$, $C^nH^{2n-10}O^4$, $C^nH^{2n-12}O^4$.

## BIATOMIC AND MONOBASIC ACIDS.

The only well-studied acids of this class are those which correspond to the general formulæ $C^nH^{2n}O^3$ and $C^nH^{2n-8}O^3$, that is to say, those belonging to the series of fatty acids and to the aromatic series. A few others are known, but they have been very imperfectly studied.

PREPARATION.—*First Process.*—These acids are prepared by submitting to the action of nitrous acid certain amides, such as glycocol and analogous bodies, obtained either by the action of ammonia on the monobrominated derivatives of monatomic acids, or by the reduction of nitrogenized monatomic acids; water and nitrogen are produced at the same time:



$$\underset{\text{Glycocol.}}{\left(\left.\begin{matrix}\left[\left.\begin{matrix}C^2H^2O'' \\ H\end{matrix}\right\}O\right]' \\ H \\ H\end{matrix}\right\}N\right)} + \underset{\text{Nitrous acid.}}{\left(\left.\begin{matrix}NO \\ H\end{matrix}\right\}O\right)}$$

$$= \underset{\text{Glycolic acid.}}{\left(\left.\begin{matrix}C^2H^2O'' \\ H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Nitrogen.}}{\left.\begin{matrix}N \\ N\end{matrix}\right\}} + \underset{\text{Water.}}{\left.\begin{matrix}H \\ H\end{matrix}\right\}O}$$

LEEDS SCHOOL OF MEDICINE

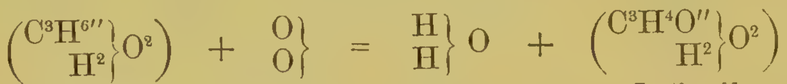
*Second Process.*—These acids are also obtained by causing moistened oxide of silver to act on the monochlorinated or monobrominated derivatives of the monatomic acids of the same series:

$$\underset{\text{Bromobutyric acid.}}{2(C^4H^7BrO^2)} + \underset{\text{Oxide of silver.}}{(Ag^2O)} + \underset{\text{Water.}}{(H^2O)} = \underset{\text{Bromide of silver.}}{2(AgBr)} + \underset{\text{Oxybutyric acid.}}{2(C^4H^8O^3)}$$

The oxide of silver may be replaced by caustic potash in this reaction.

This process does not succeed in the aromatic series, because the chlorinated or brominated acids known in this series contain their chlorine or bromine in the principal chain (*see* Phenols).

*Third Process.*—The corresponding glycols are oxidized by means of platinum black, care being taken that the oxidation proceeds slowly :



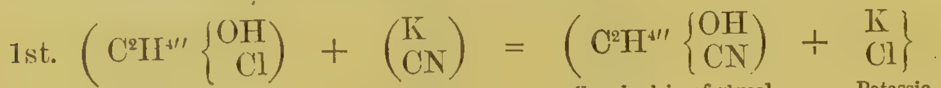
$$\left(\left.\begin{matrix}C^3H^{6\prime\prime}\\ H^2\end{matrix}\right\}O^2\right) + \left.\begin{matrix}O\\ O\end{matrix}\right\} = \left.\begin{matrix}H\\ H\end{matrix}\right\}O + \left(\left.\begin{matrix}C^3H^4O^{\prime\prime}\\ H^2\end{matrix}\right\}O^2\right)$$

Propylglycol. Oxygen. Water. Lactic acid.

But when the glycols have a molecule that is at all complicated, this cannot resist the oxidation ; an atom of carbon and two atoms of hydrogen are separated in the state of water and carbonic anhydride, and instead of the acid corresponding to the glycol employed, that which corresponds to the glycol of the lower series is obtained.

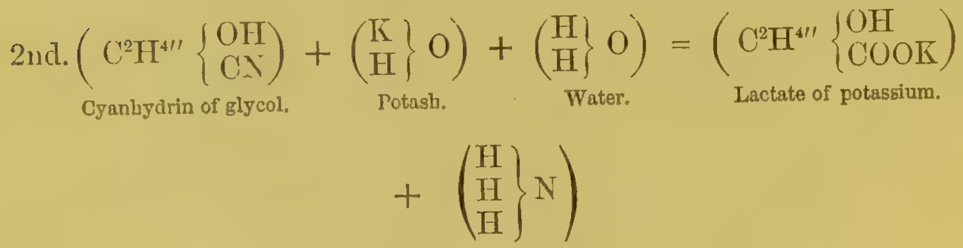
Thus the oxidation of amylglycol, instead of giving oxyvaleric acid, gives oxybutyric.

*Fourth Process.*—The monochlorhydrin of a glycol, when heated with an alcoholic solution of cyanide of potassium, gives chloride of potassium and a cyanhydrin. If this cyanhydrin be boiled with an alcoholic solution of potash, a disengagement of ammonia takes place, and there remains in solution the potassic salt of an acid which corresponds to the glycol one degree higher than the one employed. Thus, from the chlorhydrin of the glycol ($C^2H^6O^2$), lactic acid ($C^3H^6O^3$) is obtained, which corresponds to propylglycol ($C^3H^8O^2$) :



$$\text{1st.}\ \left(C^2H^{4\prime\prime}\left\{\begin{matrix}OH\\ Cl\end{matrix}\right.\right) + \left(\begin{matrix}K\\ CN\end{matrix}\right) = \left(C^2H^{4\prime\prime}\left\{\begin{matrix}OH\\ CN\end{matrix}\right.\right) + \left.\begin{matrix}K\\ Cl\end{matrix}\right\}$$

Chlorhydrin of glycol. Potassic cyanide. Cyanhydrin of glycol. Potassic chloride.

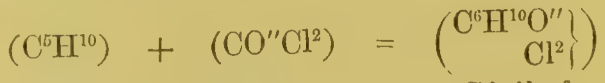


$$\text{2nd.}\left(C^2H^{4\prime\prime}\left\{\begin{matrix}OH\\ CN\end{matrix}\right.\right) + \left(\left.\begin{matrix}K\\ H\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right) = \left(C^2H^{4\prime\prime}\left\{\begin{matrix}OH\\ COOK\end{matrix}\right.\right) + \left(\left.\begin{matrix}H\\ H\\ H\end{matrix}\right\}N\right)$$

Cyanhydrin of glycol. Potash. Water. Lactate of potassium.

Ammonia.

*Fifth Process.*—When the bichlorides of the radicles of these acids are acted on by water, they are transformed into corresponding monochlorinated monatomic acids, hydrochloric acid being disengaged. Therefore, as the bodies in question can be prepared from these monochlorinated acids, it is evident that to accomplish the synthesis of the chlorides of their radicles is to accomplish their own. Lippemann has effected this synthesis by directly fixing the oxychloride of carbon on certain non-saturated hydrocarbides :



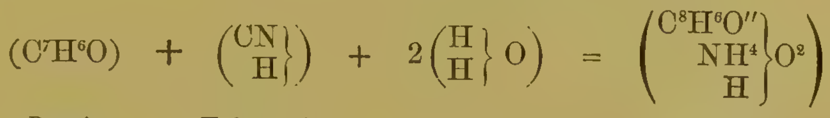
$$(C^5H^{10}) + (CO^{\prime\prime}Cl^2) = \left(\left.\begin{matrix}C^6H^{10}O^{\prime\prime}\\ Cl^2\end{matrix}\right\}\right)$$

Amylene. Oxychloride of carbon. Chloride of leucyl.

This reaction is entirely different from that which furnishes the monatomic acids by means of the oxychloride of carbon. This latter is a double decomposition, while that just given is merely a direct addition.

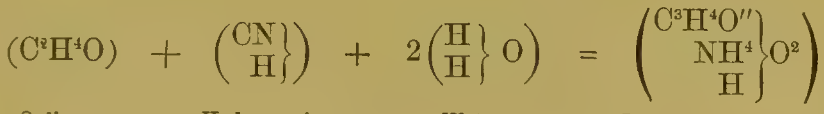
*Sixth Process.*—When a mixture of an aldehyd, water, and hydrocyanic acid is left alone for some time, there is formed the ammoniacal salt of a biatomic and monobasic acid of a series higher by one degree than that of which the aldehyd forms part. The addition of hydrochloric acid greatly assists the reaction, and is even sometimes indispensable.

Acetones may be substituted for aldehyds in this process:



$$(C^7H^6O) + \left(\left.\begin{matrix}CN\\H\end{matrix}\right\}\right) + 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}C^8H^6O''\\NH^4\\H\end{matrix}\right\}O^2\right)$$

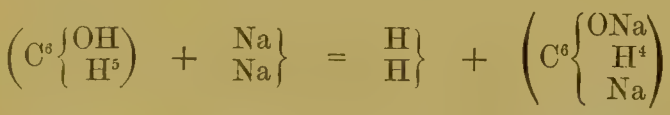
Benzoic aldehyd. Hydrocyanic acid. Water. Formobenzoylate of ammonium.



$$(C^2H^4O) + \left(\left.\begin{matrix}CN\\H\end{matrix}\right\}\right) + 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}C^3H^4O''\\NH^4\\H\end{matrix}\right\}O^2\right)$$

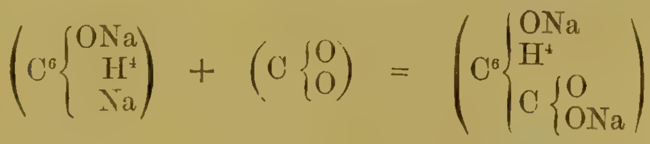
Ordinary aldehyd. Hydrocyanic acid. Water. Lactate of ammonium.

*Seventh Process.*—In the aromatic series, monobasic biatomic acids are obtained by transmitting a current of dry carbonic anhydride through a slightly-heated phenol, holding sodium in solution. In this case there is formed the sodic salt of an acid which differs from the phenol employed by the addition of $CO^2$:



$$\left(C^6\left\{\begin{matrix}OH\\H^5\end{matrix}\right.\right) + \left.\begin{matrix}Na\\Na\end{matrix}\right\} = \left.\begin{matrix}H\\H\end{matrix}\right\} + \left(C^6\left\{\begin{matrix}ONa\\H^4\\Na\end{matrix}\right.\right)$$

Phenol. Sodium. Hydrogen. Sodium-phenol.



$$\left(C^6\left\{\begin{matrix}ONa\\H^4\\Na\end{matrix}\right.\right) + \left(C\left\{\begin{matrix}O\\O\end{matrix}\right.\right) = \left(C^6\left\{\begin{matrix}ONa\\H^4\\C\left\{\begin{matrix}O\\ONa\end{matrix}\right.\end{matrix}\right.\right)$$

Sodium-phenol. Carbonic anhydride. Salicylate of sodium.

*Eighth Process.*—By causing the zinco-alcoholic compounds (zinc-ethyl and zinc-methyl) to react with the oxalate of ethyl, Frankland has succeeded in replacing an atom of oxygen in the radicle oxatyl, either by two atoms of ethyl or of methyl, or by one of each. He has thus obtained the zinco-ethylic derivatives of acids of the series $C^nH^{2n}O^3$. These compounds, when submitted to the action of water, give hydrate of zinc and the ethers of these acids, from which they may be extracted by saponification:

$$2\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}OC^2H^5\\O\\\hline O\\OC^2H^5\end{array}\right.\right) + 2\left(Zn''\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right.\right) = \left(\left.\begin{matrix}Zn''\\(C^2H^5)^2\end{matrix}\right\}O^2\right)$$

Diethylic oxalate. Zinc-ethyl. Ethylate of zinc.

$$+\left(\begin{array}{l}\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}OC^2H^5\\(C^2H^5)^2\\\hline O''\end{array}\right.\\\qquad\left.\begin{array}{l}O''\;.\;\;.\\O''\;.\;\;.\end{array}\right\}Zn''\\\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}O''\\\hline (C^2H^5)^2\\OC^2H^5\end{array}\right.\end{array}\right)$$

Zinco-leucic ether.

$$\left(\begin{array}{l}\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}OC^2H^5\\(C^2H^5)^2\\\hline O''\end{array}\right.\\\qquad\left.\begin{array}{l}O''\;.\;\;.\\O''\;.\;\;.\end{array}\right\}Zn''\\\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}O''\\\hline (C^2H^5)^2\\OC^2H^5\end{array}\right.\end{array}\right)+$$

Zinco-leucic ether.

$$2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}Zn''\\H^2\end{matrix}\right\}O^2\right) + 2\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}OC^2H^5\\(C^2H^5)^2\\\hline O\\OH\end{array}\right.\right)$$

Water. Hydrate of zinc. Leucate of ethyl (diethoxalate of ethyl).

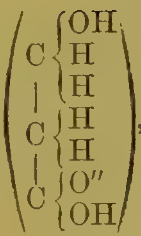
In these processes the zinco-alcoholic compounds may be replaced by a mixture of zinc and a hydriodic ether.

Are the acids obtained by these different processes identical or isomeric? The question is not yet positively decided, but it is probable that the acids prepared by Frankland's method differ from those obtained by the other methods.

As to these latter, cases of isomerism appear also to have been observed among them. Under the name of lactic acid, two acids are known, each of which answers to the formula ($C^3H^6O^3$): one exists ready formed in the flesh of animals, and is therefore called sarko-lactic acid; the other is produced by a particular fermentation of sugar of milk.

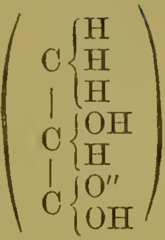
Wislicenus has recently discovered that the acid obtained by the action of potash on the cyanhydrin of glycol is identical with sarko-lactic acid, while that obtained by means of the aldehyd is identical with the lactic acid of fermentation.

This isomerism may be accounted for by supposing that sarko-lactic acid answers to the formula:



$$\left(\begin{matrix} C\left\{\begin{matrix}OH\\H\\H\end{matrix}\right.\\ | \\ C\left\{\begin{matrix}H\\H\end{matrix}\right.\\ | \\ C\left\{\begin{matrix}O''\\OH\end{matrix}\right.\end{matrix}\right)$$

, and ordinary lactic acid to the formula :

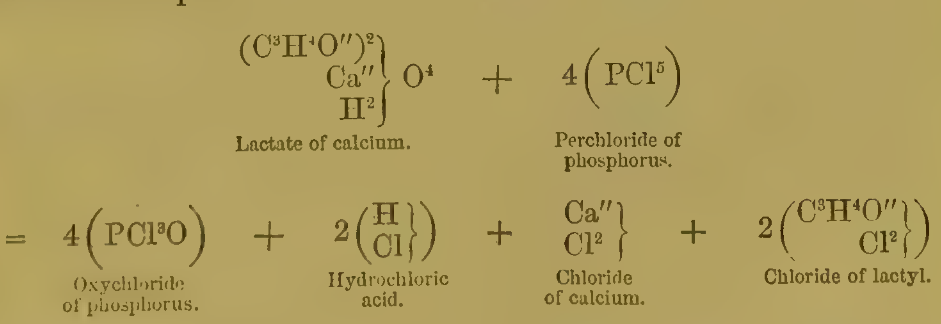


$$\left(\begin{matrix} C\left\{\begin{matrix}H\\H\\H\end{matrix}\right.\\ | \\ C\left\{\begin{matrix}OH\\H\end{matrix}\right.\\ | \\ C\left\{\begin{matrix}O''\\OH\end{matrix}\right.\end{matrix}\right)$$

It is therefore not a matter of indifference which mode of preparation is used; but at present it is not exactly known which acids the several methods furnish. This subject is worthy of further investigation.

Properties.—1st. Though biatomic, the acids of this group are only monobasic. Only one of their two atoms of typical hydrogen has well-defined basical properties; the second is alcoholic hydrogen in the fatty series, and phenic (*see* Phenols) or alcoholic in the aromatic series. These acids may therefore be regarded in the first of these series as half acids, half alcohols. In the second, they should be considered sometimes as half acids, half phenols, and sometimes as half acids, half alcohols. Thus creosotic acid ($C^8H^8O^3$) contains an acid hydrogen and a phenic hydrogen, while its isomer, formobenzoilic acid, contains an acid hydrogen and an alcoholic hydrogen. However, although their typical hydrogen cannot be replaced by positive metals under the influence of powerful bases, such as the hydrate of potassium or sodium, it seems possible to substitute certain negative elements such as tin and copper.

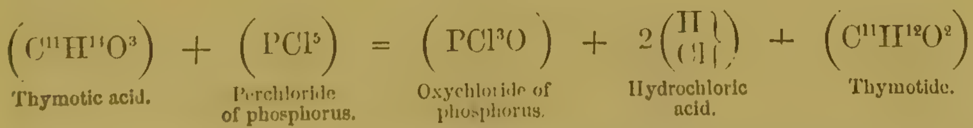
2nd. When acted upon by the perchloride of phosphorus, these acids and their salts produce a bichloride of their radicle :



$$\underset{\text{Lactate of calcium.}}{\left.\begin{matrix}(C^3H^4O'')^2\\Ca''\\H^2\end{matrix}\right\}O^4} + \underset{\text{Perchloride of phosphorus.}}{4\left(PCl^5\right)}$$

$$= \underset{\text{Oxychloride of phosphorus.}}{4\left(PCl^3O\right)} + \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Chloride of calcium.}}{\left.\begin{matrix}Ca''\\Cl^2\end{matrix}\right\}} + \underset{\text{Chloride of lactyl.}}{2\left(\left.\begin{matrix}C^3H^4O''\\Cl^2\end{matrix}\right\}\right)}$$

This reaction is not however invariable. I have shown that, under the influence of the perchloride of phosphorus, thymotic acid only loses the elements of water, giving rise to a very stable anhydride :



$$\underset{\text{Thymotic acid.}}{\left(C^{11}H^{14}O^3\right)} + \underset{\text{Perchloride of phosphorus.}}{\left(PCl^5\right)} = \underset{\text{Oxychloride of phosphorus.}}{\left(PCl^3O\right)} + \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Thymotide.}}{\left(C^{11}H^{12}O^2\right)}$$

Gerhardt had also previously observed that hydrochloric acid and an anhydride of salicylic acid are produced when this latter acid is submitted to the action, not of the perchloride, but of the oxychloride of phosphorus:

$$\underset{\text{Salicylic acid.}}{3\left(C^7H^6O^3\right)} + \underset{\text{Oxychloride of phosphorus.}}{\left(PCl^3O\right)} = \underset{\text{Phosphoric acid.}}{\left(PH^3O^4\right)} + \underset{\text{Hydrochloric acid.}}{3\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Salicylide.}}{3\left(C^7H^4O^2\right)}$$

It has been seen that the ethers of biatomic and monobasic acids prepared by Frankland's process lose $H^2O$ under the influence of terchloride of phosphorus, and are converted into the ethers of acids of another series:

$$\underset{\text{Leucate of ethyl.}}{3(C^6H^{11}(C^2H^5)O^3)} + \underset{\text{Terchloride of phosphorus.}}{(PCl^3)} = \underset{\text{Phosphorous acid.}}{(PH^3O^3)} + \underset{\text{Hydrochloric acid.}}{3(HCl)}$$
$$+ \underset{\text{Ethylic ethyl-crotonate.}}{(C^6H^9(C^2H^5)O^2)}$$

3rd. These chlorides, on contact with water, are transformed into hydrochloric acid and a monatomic chlorinated acid of the same series:

$$\underset{\text{Chloride of lactyl.}}{\left(\left.\begin{matrix}C^3H^4O''\\Cl^2\end{matrix}\right\}\right)} + \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O} = \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}} + \underset{\text{Chloro-propionic acid.}}{\left(C^3H^5ClO^2\right)}$$

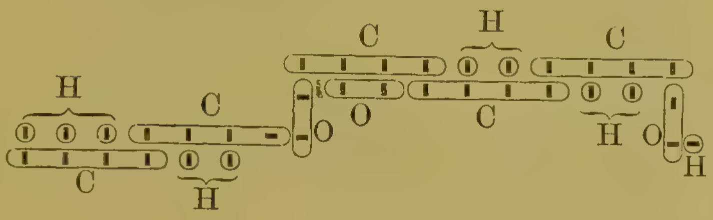
The monochlorinated acid thus obtained may undergo inverse substitution under the influence of nascent hydrogen. We then pass from one acid with three atoms of oxygen to another which only contains two atoms of this metalloid.

The reaction just mentioned may be easily explained: the chlorides of alcohol radicles resist the action of water; those of acid radicles are entirely decomposed by this liquid. The biatomic and monobasic acids participate both in the properties of alcohols and of acids; their chlorides therefore should be partially decomposed by water.

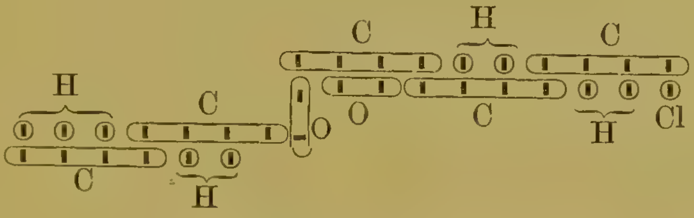
4th. When treated with alcohol, these chlorides yield hydrochloric acid, and the residue of alcohol ($C^2H^5O$), equivalent to HO, and consequently to Cl, is substituted for an atom of chlorine:

$$\underset{\text{Chloride of lactyl.}}{\left(C^3H^4O''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)} + \underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)} = \underset{\text{Chloro-lactic ether.}}{\left(C^3H^4O''\left\{\begin{matrix}Cl\\OC^2H^5\end{matrix}\right.\right)} + \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}}$$

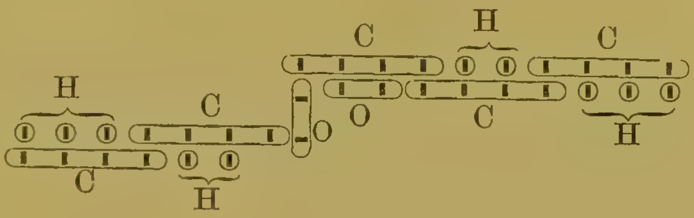
The body thus produced, according to whether we regard its relations with the acid whence it is derived or with the monatomic acid of the same series as itself, may either be called lactic ethyl-chlorhydrin, or chloro-propionic ether. In reality, it is derived from the lactate of ethyl by the substitution of Cl for OH, or from the propionate of ethyl by the substitution of Cl for H:



Lactate of ethyl.



Lactic ethyl-chlorhydrin, or chloro-propionate of ethyl.



Propionate of ethyl.

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5th. Under the influence of potash, these ethyl-chlorhydrins are transformed into a potassic salt of the original acid with chloride of potassium and alcohol:

$$\underset{\text{Chloracetic ether.}}{\left(C^3H^4O''\begin{cases}Cl\\OC^2H^5\end{cases}\right)} + \underset{\text{Potash.}}{2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic lactate.}}{\left(C^3H^4O''\begin{cases}OK\\OH\end{cases}\right)} + \underset{\text{Chloride of potassium.}}{\left.\begin{matrix}K\\Cl\end{matrix}\right\}}$$

$$+ \underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)}$$

6th. If the ethylate of sodium be made to react on these ethyl-chlorhydrins, the residue ($C^2H^5O$) is substituted for the chlorine, and a diethylic ether of the original acid is obtained:

$$\underset{\text{Chloracetic acid.}}{C^3H^4O''\begin{cases}Cl\\OC^2H^5\end{cases}\Big)} + \underset{\text{Ethylate of sodium.}}{\left(\left.\begin{matrix}C^2H^5\\Na\end{matrix}\right\}O\right)} + \underset{\text{Chloride of sodium.}}{\left.\begin{matrix}Na\\Cl\end{matrix}\right\}} + \underset{\text{Diethylic lactate.}}{\left(C^3H^4O''\begin{cases}OC^2H^5\\OC^2H^5\end{cases}\right)}$$

7th. The diethylic ethers of these acids, acted upon by potash, give lcohol and the alkaline salt of an acid ether, which an excess of lkali does not saponify, and which may be easily separated from its alt:

$$\underset{\text{Diethylic lactate.}}{\left(C^3H^4O''\left\{\begin{matrix}OC^2H^5\\OC^2H^5\end{matrix}\right.\right)} + \underset{\text{Potash.}}{\left.\begin{matrix}K\\H\end{matrix}\right\}O} = \underset{\text{Ethyl-lactate of potassium.}}{\left(C^3H^4O''\left\{\begin{matrix}OC^2H^5\\OK\end{matrix}\right.\right)} + \underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)}$$

It will be readily supposed that the second molecule of ethyl cannot be eliminated by means of potash, as the acids in question are not capable of forming dipotassic salts.

8th. On causing the acids of this class to act directly on alcohol, or by distilling one of their salts with an alkaline sulphovinate, a neutral monethylic ether is obtained which is isomeric with the acid monethylic ether the mode of formation of which has just been described:

$$\underset{\text{Potassic ethyl-sulphate.}}{\left(SO^{2''}\left\{\begin{matrix}OC^2H^5\\OK\end{matrix}\right.\right)} + \underset{\text{Potassic lactate.}}{\left(C^3H^4O''\left\{\begin{matrix}OH\\OK\end{matrix}\right.\right)} = \underset{\text{Neutral sulphate of potassium.}}{\left(SO^{2''}\left\{\begin{matrix}OK\\OK\end{matrix}\right.\right)}$$

$$+ \underset{\text{Monethylic lactate.}}{\left(C^3H^4O''\left\{\begin{matrix}OH\\OC^2H^5\end{matrix}\right.\right)}$$

It must be supposed that in these ethers which possess acid properties, ethyl is substituted for the alcoholic hydrogen, while in those that are neutral, the ethyl is substituted for the positive hydrogen. This is shown by the last equation, in which the ethyl is seen to be substituted for potassium.

9th. Neutral monethylic ethers, submitted to the action of metallic potassium, disengage hydrogen and give rise to potassic derivatives, isomeric with the potassic salts of acid ethers:

$$2\underset{\text{Monethylic lactate.}}{\left(C^3H^4O''\left\{\begin{matrix}OH\\OC^2H^5\end{matrix}\right.\right)} + \underset{\text{Potassium.}}{\left.\begin{matrix}K\\K\end{matrix}\right\}} = \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}} + 2\underset{\text{Potassic monethylic lactate.}}{\left(C^3H^4O''\left\{\begin{matrix}OK\\OC^2H^5\end{matrix}\right.\right)}$$

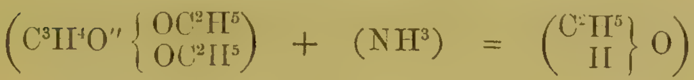
The potassic monethylic lactate is isomeric with the ethyl-lactate of potassium $\left(C^3H^4O''\left\{\begin{matrix}OC^2H^5\\OK\end{matrix}\right.\right)$.

The potassic derivatives of neutral monethylic ethers, treated by iodide of ethyl, give potassic iodide and diethylic ethers. An analogous result is obtained by submitting the argentic salts of acid ethers to the action of iodide of ethyl:

$$\underset{\text{Monethylic lactate of potassium.}}{\left(C^3H^4O''\left\{\begin{matrix}OK\\OC^2H^5\end{matrix}\right.\right)} + \underset{\text{Iodide of ethyl.}}{\left(\left.\begin{matrix}C^2H^5\\I\end{matrix}\right\}\right)} = \underset{\text{Iodide of potassium.}}{\left.\begin{matrix}K\\I\end{matrix}\right\}} + \underset{\text{Diethylic lactate.}}{\left(C^3H^4O''\left\{\begin{matrix}OC^2H^5\\OC^2H^5\end{matrix}\right.\right)}$$

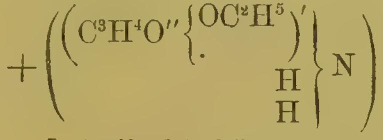
$$\underset{\text{Ethyl-lactate of silver.}}{\left(C^3H^4O''\left\{\begin{matrix}OC^2H^5\\OAg\end{matrix}\right.\right)} + \underset{\text{Iodide of ethyl.}}{\left(\left.\begin{matrix}C^2H^5\\I\end{matrix}\right\}\right)} = \underset{\text{Iodide of silver.}}{\left.\begin{matrix}Ag\\I\end{matrix}\right\}} + \underset{\text{Diethylic lactate.}}{\left(C^3H^4O''\left\{\begin{matrix}OC^2H^5\\OC^2H^5\end{matrix}\right.\right)}$$

10th. Submitted to the action of an alcoholic solution of ammonia, the diethylic ethers give alcohol and the ethers of acid amides:



$$\left(C^3H^4O''\left\{\begin{matrix}OC^2H^5\\OC^2H^5\end{matrix}\right.\right) + (NH^3) = \left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)$$

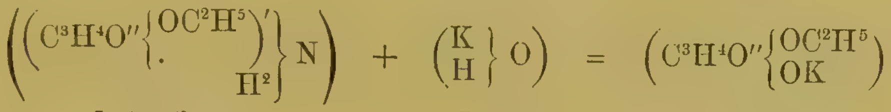
Diethylic lactate. Ammonia. Alcohol.



$$+\left(\left.\begin{matrix}\left(C^3H^4O''\left\{\begin{matrix}OC^2H^5\\ .\end{matrix}\right.\right)'\\H\\H\end{matrix}\right\}N\right)$$

Lactamide of ethyl (lactamethane).

These new bodies, under the influence of alkalies, are transformed into ammonia and salts of acid monethylic ethers:



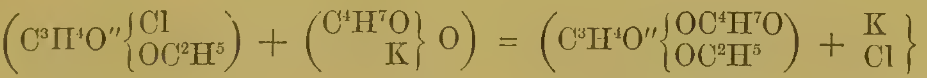
$$\left(\left.\begin{matrix}\left(C^3H^4O''\left\{\begin{matrix}OC^2H^5\\ .\end{matrix}\right.\right)'\\H^2\end{matrix}\right\}N\right) + \left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right) = \left(C^3H^4O''\left\{\begin{matrix}OC^2H^5\\OK\end{matrix}\right.\right)$$

Lactamethane. Potash. Ethyl-lactate of potassium.

$$+ (NH^3)$$

Ammonia.

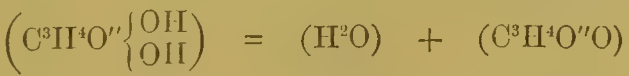
11th. On causing the butyrate of potassium to act on the chlorinated acids obtained by the action of water on the bichlorides of the radicles of biatomic monobasic acids, bodies are obtained which are derived from these acids by the substitution of butyryl for hydrogen. These bodies are instable; but if the ethyl-chlorhydrins of these acids be substituted for their chlorhydrins, stable butyro-ethylic ethers are formed, which alkalies split up into alcohol, butyrate, and the alkaline salt of the biatomic acid which enters into their composition:



$$\left(C^3H^4O''\left\{\begin{matrix}Cl\\OC^2H^5\end{matrix}\right.\right) + \left(\left.\begin{matrix}C^4H^7O\\K\end{matrix}\right\}O\right) = \left(C^3H^4O''\left\{\begin{matrix}OC^4H^7O\\OC^2H^5\end{matrix}\right.\right) + \left.\begin{matrix}K\\Cl\end{matrix}\right\}$$

Lactic ethyl-chlorhydrin. Potassic butyrate. Lactobutyrate of ethyl. Chloride of potassium.

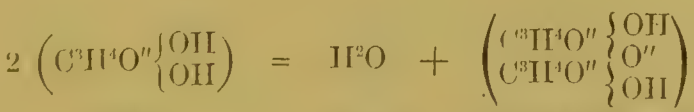
12th. When submitted to the influence of heat, biatomic monobasic acids lose a molecule of water and furnish an anhydride:



$$\left(C^3H^4O''\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right) = (H^2O) + (C^3H^4O''O)$$

Lactic acid. Water. Lactide (lactic anhydride).

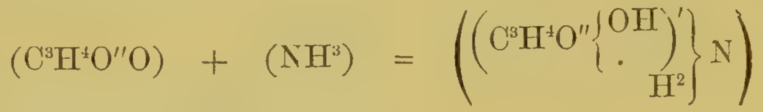
When the heat is applied carefully, the elimination of water takes place at the cost of two molecules of acid, and a condensed acid is obtained:



$$2\left(C^3H^4O''\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right) = H^2O + \left(\begin{matrix}C^3H^4O''\\C^3H^4O''\end{matrix}\begin{matrix}\left\{\begin{matrix}OH\\O''\end{matrix}\right.\\\left\{\begin{matrix}\\OH\end{matrix}\right.\end{matrix}\right)$$

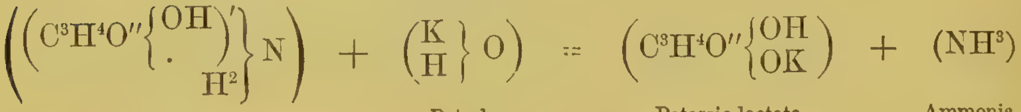
Lactic acid. Water. Dilactic acid (formerly called anhydrous lactic acid).

13th. The anhydrides, treated with ammoniacal gas, furnish amides, which potash decomposes with disengagement of ammonia and production of a potassic salt:



$$(C^3H^4O''O) + (NH^3) = \left(\left.\begin{matrix}\left(C^3H^4O''\left\{\begin{matrix}OH\\ \cdot\end{matrix}\right.\right)'\\ H^2\end{matrix}\right\}N\right)$$

Lactic anhydride. Ammonia. Lactamide.

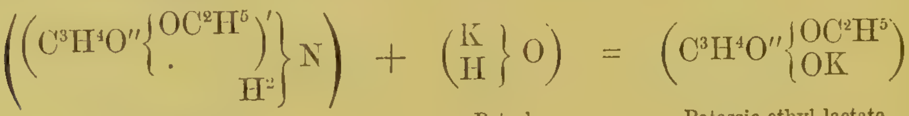


$$\left(\left.\begin{matrix}\left(C^3H^4O''\left\{\begin{matrix}OH\\ \cdot\end{matrix}\right.\right)'\\ H^2\end{matrix}\right\}N\right) + \left(\left.\begin{matrix}K\\ H\end{matrix}\right\}O\right) = \left(C^3H^4O''\left\{\begin{matrix}OH\\ OK\end{matrix}\right.\right) + (NH^3)$$

Lactamide. Potash. Potassic lactate. Ammonia.

All the attempts hitherto made to obtain amides derived from two molecules of ammonia have failed, though the biatomicity of these acids renders the existence of such bodies very probable.

14th. Ethylamine also reacts on these anhydrides. The amides which are formed are isomeric with the amidated ethers produced by means of diethylic ethers and ammonia. While these latter give an acid ether and ammonia, under the influence of alkalies, the former in this case disengage ethylamine, and the acid is reformed:

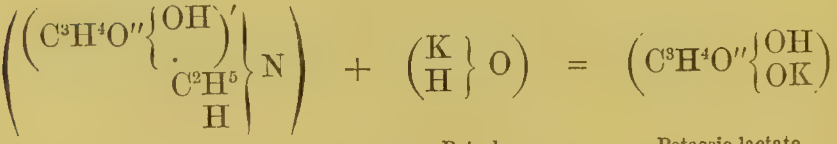


$$\left(\left.\begin{matrix}\left(C^3H^4O''\left\{\begin{matrix}OC^2H^5\\ \cdot\end{matrix}\right.\right)'\\ H^2\end{matrix}\right\}N\right) + \left(\left.\begin{matrix}K\\ H\end{matrix}\right\}O\right) = \left(C^3H^4O''\left\{\begin{matrix}OC^2H^5\\ OK\end{matrix}\right.\right)$$

Lactamethane. Potash. Potassic ethyl-lactate.

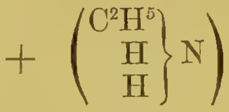
$$+ (NH^3)$$

Ammonia.



$$\left(\left.\begin{matrix}\left(C^3H^4O''\left\{\begin{matrix}OH\\ \cdot\end{matrix}\right.\right)'\\ C^2H^5\\ H\end{matrix}\right\}N\right) + \left(\left.\begin{matrix}K\\ H\end{matrix}\right\}O\right) = \left(C^3H^4O''\left\{\begin{matrix}OH\\ OK\end{matrix}\right.\right)$$

Lactethylamide. Potash. Potassic lactate.



$$+ \left(\left.\begin{matrix}C^2H^5\\ H\\ H\end{matrix}\right\}N\right)$$

Ethylamine.

It has been seen that, when ammonia acts on monochlorinated or monobrominated monatomic acids, an amide is obtained of the biatomic monobasic acid of the same series. This amide is acid, and isomeric with that produced in the action of ammonia on the anhydrides of these latter acids, this being neutral.

In order to understand the isomerism of these two amides, it should be considered that the monamides of the acids in question represent a molecule of ammonia in which H is replaced by a monatomic residue, derived from these acids by the elimination of OH; hence, if the group OH eliminated contain the alcoholic hydrogen, that which enters into the molecule of ammonia as an integral part of the residue contains positive hydrogen, and an acid amide is produced. In the contrary case the amide contains the alcoholic hydrogen, and is neutral. On placing the signs + and − against the two atoms of hydrogen to indicate which is positive and which is negative, formulæ may be obtained which give a clear idea of this isomerism:

$$\left(C^2H^2O''\left\{\begin{matrix}OH-\\OH+\end{matrix}\right.\right) \quad - \quad OH- \quad = \quad \left(C^2H^2O''\left\{\begin{matrix}\cdot\\OH+\end{matrix}\right.\right)'$$

Glycolic acid. Monatomic residue.

This monatomic residue, substituted for H in ammonia, gives the amide $\left.\begin{matrix}\left(C^2H^2O''\left\{\begin{matrix}\cdot\\OH+\end{matrix}\right.\right)'\\H^2\end{matrix}\right\}N$, which contains a positive hydrogen, and therefore acts as acid. This amide is glycocol.

On the contrary, if the group OH+ be subtracted from glycolic acid there remains the residue $\left(C^2H^2O''\left\{\begin{matrix}\cdot\\OH-\end{matrix}\right.\right)'$, which when substituted for hydrogen of ammonia, furnishes an amide which no longer contains positive hydrogen, and which therefore is neutral.

15th. When the acids of this group are acted upon by hydrochloric or by hydrobromic acid, water is formed; the group HO which contains the alcoholic hydrogen is eliminated, and chlorine or bromine is introduced into the molecule; in this case there is formed a chlorinated or brominated derivative of the monatomic acid of the same series:

$$\left(C^3H^4O''\left\{\begin{matrix}OH-\\OH+\end{matrix}\right.\right) + \left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right) = \left(\left.\begin{matrix}H-\\H\end{matrix}\right\}O\right) + \left(C^3H^4ClO,H+O\right)$$

Lactic acid. Hydrochloric acid. Water. Chloro-propionic acid.

16th. Hydriodic acid does not produce an iodized derivative, but it reduces the biatomic acid to a lower degree of oxidation, thus transforming it into a monatomic acid. According to Kékulé, a similar reaction at first takes place as with hydrochloric or hydrobromic acid, but the hydriodic acid afterwards reacts on the iodized acid produced, iodine is set free, and there remains a monatomic acid which is not iodized:

First Stage.

$$\left(C^3H^4O''\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right) + \left.\begin{matrix}H\\I\end{matrix}\right\} = (C^3H^4IO,OH) + (H^2O)$$

Lactic acid. Hydriodic acid. Iodo-propionic acid. Water.

Second Stage.

$$\left(C^3H^4IO,OH\right) + \left.\begin{matrix}H\\I\end{matrix}\right\} = \left.\begin{matrix}I\\I\end{matrix}\right\} + (C^3H^5O,OH)$$

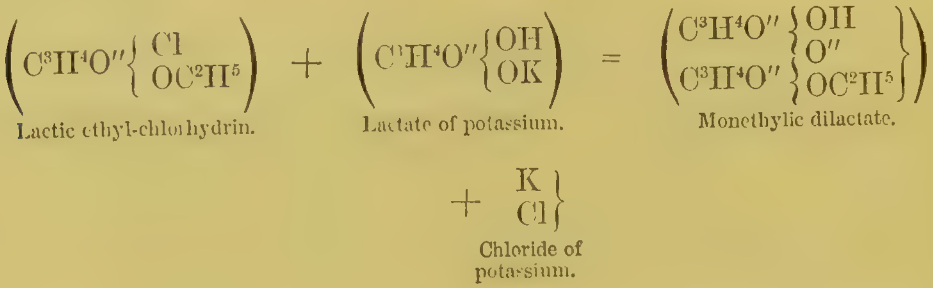
Iodo-propionic acid. Hydriodic acid. Iodine. Propionic acid.

Kékulé has shown, as will be remembered, that all iodized derivatives under the influence of hydriodic acid undergo a double decomposition analogous to the preceding.

The biatomic and monobasic aromatic acids which contain a phenic hydrogen are not reduced by hydriodic acid; those which contain an alcoholic hydrogen are reduced as in the fatty series.

**Condensed Acids derived from Biatomic and Monobasic Acids.**—As biatomic alcohols can form condensed compounds, the composition of which represents $n$ molecules of alcohol united into one with elimination of $n-1$ molecules of water, so the polyatomic acids can give rise to more condensed acids in which the polyatomic radicle of the acid is accumulated, the different radicles being united together by oxygen.

A monethylic ether of the first condensed acid is obtained by treating the potassic salt of the ordinary acid by ethyl-chlorhydrin of the same body:

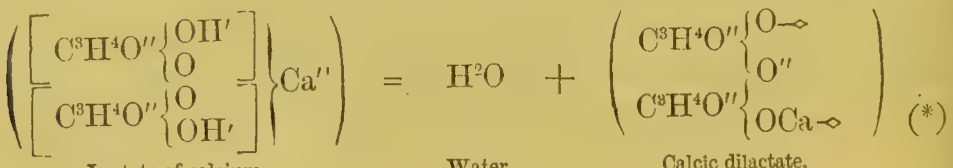


$$\left(C^3H^4O''\left\{\begin{matrix}Cl\\OC^2H^5\end{matrix}\right.\right) + \left(C^3H^4O''\left\{\begin{matrix}OH\\OK\end{matrix}\right.\right) = \left(\begin{matrix}C^3H^4O''\left\{\begin{matrix}OH\\O''\end{matrix}\right.\\C^3H^4O''\left\{OC^2H^5\right.\end{matrix}\right) + \left.\begin{matrix}K\\Cl\end{matrix}\right\}$$

Lactic ethyl-chlorhydrin. Lactate of potassium. Monethylic dilactate. Chloride of potassium.

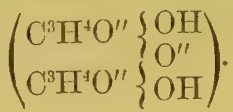
It is very probable that if, in this operation, the potassic salt of ethylic ether were substituted for that of the ordinary acid, the diethylic ether of the first condensed acid would be obtained.

A calcic salt of a condensed acid of the first degree, may be produced by submitting the calcic salt of the ordinary acid to the action of heat:



$$\left(\left.\begin{matrix}\left[C^3H^4O''\left\{\begin{matrix}OH'\\O\end{matrix}\right.\right]\\\left[C^3H^4O''\left\{\begin{matrix}O\\OH'\end{matrix}\right.\right]\end{matrix}\right\}Ca''\right) = H^2O + \left(\begin{matrix}C^3H^4O''\left\{\begin{matrix}O\multimap\\O''\end{matrix}\right.\\C^3H^4O''\left\{OCa\multimap\right.\end{matrix}\right) \quad (*)$$

Lactate of calcium. Water. Calcic dilactate.

The condensed acid whence these different products are derived has not as yet been obtained in a free state; but M. Pelouze states that by the gentle action of heat on lactic acid a body is produced which he calls anhydrous lactic acid  $\left(\begin{matrix}C^3H^4O''\left\{\begin{matrix}OH\\O''\end{matrix}\right.\\C^3H^4O''\left\{OH\right.\end{matrix}\right)$. According to our ideas, this is dilactic acid.

Bodies are known which contain three acid radicles in a second degree of condensation. They are formed at the same time as the condensed products of the first degree, when an ethyl-chlorhydrin acts on a salt of potassium. Thus, in the example given, besides the monethylic dilactate, there is also formed a diethylic trilactate

$$\left(\begin{array}{ll} C^3H^4O'' & \left\{\begin{array}{l} OC^2H^5 \\ O'' \end{array}\right. \\ C^3H^4O'' & \left\{\begin{array}{l} O'' \end{array}\right. \\ C^3H^4O'' & \left\{\begin{array}{l} OC^2H^5 \end{array}\right. \end{array}\right).$$

The formation of these bodies by the reaction of a second molecule of ethyl-chlorhydrin on the first product of condensation will be readily understood:

$$\left(\begin{array}{ll} C^3H^4O'' & \left\{\begin{array}{l} OH \\ O'' \end{array}\right. \\ C^3H^4O'' & \left\{\begin{array}{l} OC^2H^5 \end{array}\right. \end{array}\right\}\right) + \left(C^3H^4O''\left\{\begin{array}{l} Cl \\ OC^2H^5 \end{array}\right.\right) = \left.\begin{array}{l} H \\ Cl \end{array}\right\}$$

Monethylic dilactate. Lactic ethyl-chlorhydrin. Hydrochloric acid.

$$+ \left(\begin{array}{ll} C^3H^4O'' & \left\{\begin{array}{l} OC^2H^5 \\ O'' \end{array}\right. \\ C^3H^4O'' & \left\{\begin{array}{l} O'' \end{array}\right. \\ C^3H^4O'' & \left\{\begin{array}{l} OC^2H^5 \end{array}\right. \end{array}\right\}\right)$$

Diethylic trilactate.

The same bodies may also be prepared by causing the anhydride of an acid of this group to act on the diethylic ether of the same acid:

$$2\left(C^3H^4O''O\right) + \left(C^3H^4O''\left\{\begin{array}{l} OC^2H^5 \\ OC^2H^5 \end{array}\right.\right) = \left(\begin{array}{ll} C^3H^4O'' & \left\{\begin{array}{l} OC^2H^5 \\ O'' \end{array}\right. \\ C^3H^4O'' & \left\{\begin{array}{l} O'' \end{array}\right. \\ C^3H^4O'' & \left\{\begin{array}{l} OC^2H^5 \end{array}\right. \end{array}\right\}\right)$$

Lactic anhydride. Diethylic lactate. Diethylic trilactate.

By the action of the ethyl-chlorhydrin of an acid on a potassic salt of another acid, mixed condensed acids may be obtained which contain the radicles not only of two distinct acids, but also of two acids belonging to two different groups:

$$2\left(C^3H^4O''\left\{\begin{array}{l} Cl \\ OC^2H^5 \end{array}\right.\right) + \left(C^4H^4O^{2''}\left\{\begin{array}{l} OK \\ OK \end{array}\right.\right) = \left(\begin{array}{ll} C^3H^4O'' & \left\{\begin{array}{l} OC^2H^5 \\ O'' \end{array}\right. \\ C^4H^4O^{2''} & \left\{\begin{array}{l} O'' \end{array}\right. \\ C^3H^4O'' & \left\{\begin{array}{l} OC^2H^5 \end{array}\right. \end{array}\right\}\right)$$

Lactic ethyl-chlorhydrin. Succinate of potassium. Diethylic lacto-succinate.

$$+ \quad 2\left(\left.\begin{array}{l} K \\ Cl \end{array}\right\}\right)$$

Chloride of potassium.

It will be seen that the reactions which give rise to these condensed products are the same as those which give rise to the derivatives of condensation of the glycols.

Thus, while the di- and tri-ethylenic alcohols are obtained by the reaction of the oxide of ethylene or bromhydrin on glycol, the ethylic dilactate and the diethylic trilactate are obtained by the reaction of lactic ether on lactide, or of lactate of potassium on the lactic ethyl-chlorhydrin.

$$\text{1st.}\quad \underset{\text{Glycol.}}{\left(C^2H^{4\prime\prime}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)} + \underset{\text{Oxide of ethylene.}}{2\left(C^2H^4O\right)} = \underset{\text{Triethylenic glycol.}}{\left(\begin{matrix}C^2H^{4\prime\prime}\\C^2H^{4\prime\prime}\\C^2H^{4\prime\prime}\end{matrix}\left\{\begin{matrix}OH\\O''\\O''\\OH\end{matrix}\right.\right)}$$

$$\underset{\text{Lactic ether.}}{\left(C^3H^4O''\left\{\begin{matrix}OC^2H^5\\OC^2H^5\end{matrix}\right.\right)} + \underset{\text{Lactide.}}{2\left(C^3H^4O^2\right)} = \underset{\text{Diethylic trilactate.}}{\left(\begin{matrix}C^3H^4O''\\C^3H^4O''\\C^3H^4O''\end{matrix}\left\{\begin{matrix}OC^2H^5\\O''\\O''\\OC^2H^5\end{matrix}\right.\right)}$$

$$\text{2nd.}\ \underset{\text{Glycol.}}{\left(C^2H^{4\prime\prime}\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)} + \underset{\text{Chlorhydrin.}}{\left(C^2H^{4\prime\prime}\left\{\begin{matrix}Cl\\OH\end{matrix}\right.\right)} = \underset{\text{Diethylenic glycol.}}{\left(\begin{matrix}C^2H^{4\prime\prime}\\C^2H^{4\prime\prime}\end{matrix}\left\{\begin{matrix}OH\\O''\\OH\end{matrix}\right\}\right)} + \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}}$$

$$\underset{\text{Potassic lactate.}}{\left(C^3H^4O''\left\{\begin{matrix}OH\\OK\end{matrix}\right.\right)} + \underset{\text{Chloracetic ether.}}{\left(C^3H^4O''\left\{\begin{matrix}Cl\\OC^2H^5\end{matrix}\right.\right)} = \underset{\text{Monethylic dilactate.}}{\left(\begin{matrix}C^3H^4O''\\C^3H^4O''\end{matrix}\left\{\begin{matrix}OH\\O''\\OC^2H^5\end{matrix}\right\}\right)}$$

$$+\ \underset{\text{Chloride of potassium.}}{\left.\begin{matrix}Cl\\K\end{matrix}\right\}}$$

$$\underset{\text{Diethylenic glycol.}}{\left(\begin{matrix}C^2H^{4\prime\prime}\\C^2H^{4\prime\prime}\end{matrix}\left\{\begin{matrix}OH\\O''\\OH\end{matrix}\right\}\right)} + \underset{\text{Chlorhydrin of glycol.}}{\left(C^2H^{4\prime\prime}\left\{\begin{matrix}Cl\\OH\end{matrix}\right.\right)} = \underset{\text{Triethylenic glycol.}}{\left(\begin{matrix}C^2H^{4\prime\prime}\\C^2H^{4\prime\prime}\\C^2H^{4\prime\prime}\end{matrix}\left\{\begin{matrix}OH\\O''\\O''\\OH\end{matrix}\right\}\right)} + \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}}$$

$$\underset{\text{Monethylic dilactate.}}{\left(\begin{matrix}C^3H^4O''\\C^3H^4O''\end{matrix}\left\{\begin{matrix}OH\\O''\\OC^2H^5\end{matrix}\right\}\right)} + \underset{\text{Lactic ethyl-chlorhydrin.}}{\left(C^3H^4O''\left\{\begin{matrix}Cl\\OC^2H^5\end{matrix}\right.\right)} = \underset{\text{Diethylic trilactate.}}{\left(\begin{matrix}C^3H^4O''\\C^3H^4O''\\C^3H^4O''\end{matrix}\left\{\begin{matrix}OC^2H^5\\O''\\O''\\OC^2H^5\end{matrix}\right\}\right)}$$

$$+\ \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}}$$

Wurtz has obtained a diglycolic acid $\left(\begin{matrix}C^2H^2O''\\C^2H^2O''\end{matrix}\left\{\begin{matrix}OH\\O''\\OH\end{matrix}\right\}\right)$ by oxidizing the diethylenic glycol $\left(\begin{matrix}C^2H^{4\prime\prime}\\C^2H^{4\prime\prime}\end{matrix}\left\{\begin{matrix}OH\\O''\\OH\end{matrix}\right\}\right)$. Is this acid the homologue of dilactic acid, the ethylic ethers of which are known? This point is not yet decided. The instability of dilactic acid, which cannot be isolated from its combinations, and the greater stability of the acid prepared by means of the diethylenic glycol, would cause the homology of these bodies to be doubted. It is possible that the acid called by Wurtz diglycolic is the oxalo-ethylenic acid, and has for formula, not $\left(\begin{matrix}C^2H^2O'' \\ C^2H^2O''\end{matrix}\left\{\begin{matrix}OH \\ O'' \\ OH\end{matrix}\right\}\right)$ but $\left(\begin{matrix}C^2O^{2''} \\ C^2H^{4''}\end{matrix}\left\{\begin{matrix}OH \\ O'' \\ OH\end{matrix}\right\}\right)$. Remembering that, in the oxidation of triethylenic glycol, it is not possible to introduce more than two atoms of oxygen by substitution, though this glycol contains three molecules of ethylene in which substitution might be effected, we shall be tempted to agree with the second hypothesis, as it better accounts for the difference of properties which exists between dilactic acid and the acid hitherto called diglycolic. This question can only be solved by oxidizing dipropylenic glycol, and seeing whether the acid obtained gives derivatives which are identical or isomeric with those obtained directly by means of lactic acid.

The first term of the series of acids corresponding to the general formula $C^nH^{2n}O^3$ would be carbonic acid $CH^2O^3$, which would present the same relations towards the unknown methylenic glycol as glycolic acid presents towards ordinary glycol.

Carbonic acid does not exist; only its anhydride is known; but as with alkaline bases this anhydride gives salts containing two atoms of metal, it is evident that carbonic acid, if it existed, would be bibasic as well as biatomic, while its homologues are only monobasic. In the general remarks on basicity and atomicity, we will endeavour to explain this anomaly.

**Acids known in this group.**—We know: 1st. *In the series* $C^nH^{2n}O^3$:

Glycolic acid $C^2H^4O^3$, corresponding to glycol $C^2H^6O^2$.

Lactic acid $C^3H^6O^3$, corresponding to propylglycol $C^3H^8O^2$.

Oxybutyric acid $C^4H^8O^3$, and its isomer dimethoxalic acid, corresponding, the first to butylglycol $C^4H^{10}O^2$, the second to an unknown isomer of this.

Ethomethoxalic acid $C^5H^{10}O^3$, isomeric with oxyvaleric acid, which is derived from amylglycol $C^5H^{12}O^2$; the glycol which corresponds to dimethoxalic acid is unknown, it would have the formula $C^5H^{12}O^2$.

Leucic acid and its isomer diethoxalic acid $C^6H^{12}O^3$ are derived, the first from hexylglycol $C^6H^{14}O^2$, and the second from an unknown isomer of this alcohol.

To lactic acid there corresponds an isomer, sarkolactic acid, and perhaps others besides. Oxybutyric acid has also been called, according to the manner in which it has been prepared, butylactic acid and acetonic acid. It is not yet decided whether these different names apply to one single acid or to isomers.

2nd. *In the series* $C^nH^{2n-2}O^3$:

Pyruvic acid $C^3H^4O^3$, corresponding to a glycol $C^3H^6O^2$*.

Roccellic acid $C^{12}H^{22}O^3$, corresponding to a glycol $C^{12}H^{24}O^2$*.

Ricinoleic acid $C^{18}H^{34}O^3$, corresponding to a glycol $C^{18}H^{36}O^2$*.

3rd. *In the series* $C^nH^{2n-4}O^3$ :

Guiacic acid $C^6H^8O^3$, corresponding to a glycol $C^6H^{10}O^2$*.

4th. *In the series* $C^nH^{2n-6}O^3$ :

No acid is as yet known.

5th. *In the series* $C^nH^{2n-8}O^3$ :

Salicylic acid, oxybenzoic acid, and par-oxybenzoic acid $C^7H^6O^3$, which correspond, the first to saligenin $C^7H^8O^2$, and the two others to two unknown isomers of this body.

Formobenzoylic acid, creosotic acid, and anisic acid $C^8H^8O^3$, which correspond, the first to an unknown tollyl-glycol, the second to an unknown homologue of saligenin, and the third to anisic alcohol $C^8H^{10}O^2$.

An acid $C^9H^{10}O^3$ obtained by the action of potash on the cyanhydrin of anisic alcohol, corresponding to an unknown xylenyl-glycol $C^9H^{12}O^2$*.

Phloretic acid $C^{10}H^{12}O^3$, corresponding to a homologue of saligenin $C^{10}H^{14}O^2$*.

Thymotic acid $C^{11}H^{14}O^3$, corresponding to thymosaligenin $C^{11}H^{16}O^2$*.

Anisic acid is the same as methyl-paroxybenzoic acid : in fact, under many circumstances the methyl group is detached from this acid, which only contains a single atom of hydroxyl (OH), and which Ladenburg has obtained synthetically by substituting $CH^3$ for H in par-oxybenzoic acid. The acid $C^9H^{10}O^3$, which has only been obtained by the action of alkalies on a cyanhydric ether, should not only be isomeric with the true homologue of the oxybenzoic and formo-benzoylic acids, but also with the homologue of anisic acid itself.

6th. *In the series* $C^nH^{2n-10}O^3$ :

Coumaric acid $C^9H^8O^3$, corresponding to cinnamyl-glycol $C^9H^{10}O^2$*.

7th. *In the series* $C^nH^{2n-12}O^3$, and

8th. *In the series* $C^nH^{2n-14}O^3$ :

No acid is as yet known.

9th. *In the series* $C^nH^{2n-16}O^3$ :

Benzilic acid $C^{14}H^{12}O^3$, corresponding to the glycol $C^{14}H^{14}O^2$, which, as M. Grimaux observes, would be to benzoic aldehyd what pinakone is to acetone. This glycol might be hydrobenzoin :

$$2\underset{\text{Acetone.}}{(C^3H^6O)} + \underset{\text{Hydrogen.}}{H^2} = \underset{\text{Pinakone.}}{(C^6H^{14}O^2)}$$

$$2\underset{\substack{\text{Benzoic}\\\text{aldehyd.}}}{(C^7H^6O)} + \underset{\text{Hydrogen.}}{H^2} = \underset{\text{Benzilic glycol.}}{(C^{14}H^{14}O^2)}$$

SCHOOL OF MEDIC

## STUDY OF THE MOST IMPORTANT OF THESE ACIDS.

**Lactic Acid** $\left(C^3H^4O''\left\{\begin{matrix}OH-\\OH+\end{matrix}\right.\right)$.—Lactic acid may be obtained by several processes, and has been found ready formed in the flesh of animals. However, the acid which impregnates the muscles is not identical but simply isomeric with that which is produced by means of fermentation, and which is better known.

PREPARATION.—1st. Lactic acid is formed in a particular fermentation of the different kinds of sugar, starch and analogous substances, and is usually procured by this means. For this purpose water, cane-sugar, curdled skim-milk, tartaric acid, and decayed cheese are mixed in the proportions mentioned for butyric acid, and the mixture is kept at a temperature of 30° or 35°, and stirred several times daily. At the end of about ten days it is found as a thick mass of lactate of calcium. Then ten kilogrammes of boiling water and fifteen grammes of caustic lime are added, and the whole is boiled for half an hour and passed through a linen cloth.

The liquid evaporated almost to dryness, and left alone for four or five days, deposits crystalline lactate of calcium. This salt is pressed, diluted with a tenth part of its weight of hot water, and again pressed, this operation being repeated two or three times.

When the calcic lactate is sufficiently dry. it is dissolved in twice its weight of boiling water, and 210 grammes of sulphuric acid for each kilogramme of calcic salt are added to the solution, the acid being previously diluted with its weight of water. An abundant precipitate of calcic sulphate forms, and is separated by filtering the liquid while still warm through a cloth. To this liquid are added 289 grammes of carbonate of zinc for each 210 grammes of sulphuric acid employed, and it is then boiled for a quarter of an hour, and filtered while boiling; lactate of zinc is deposited in crystals on the cooling of the liquid, and is washed in cold water to free it from the small quantity of sulphate with which it is mixed. The boiling of the lactic acid with carbonate of zinc should not be prolonged more than a quarter of an hour; if it were, a sub-salt, somewhat soluble, would be formed, and a portion of the product thereby lost.

The pure lactate of zinc, dissolved in seven and a half times its weight of boiling water, is treated with a current of hydrosulphuric acid until sulphide of zinc is no longer precipitated, even after the solution has become cold. This is filtered, boiled to free it from the sulphuretted hydrogen it contains, and then evaporated over a water-bath to the consistence of syrup.

When lactic acid is prepared by fermenting sugar, it is necessary to arrest the fermentation when the mass has become thick, or the lactic would be converted into butyric acid.

2nd. Lactic acid is formed when a current of nitrous acid is passed through an aqueous solution of alanine:

$$\underset{\text{Alanine.}}{\left(\left.\begin{matrix}\left(\left.\begin{matrix}C^3H^4O'' \\ H\end{matrix}\right\} O\right)' \\ H^2\end{matrix}\right\} N\right)} + \underset{\text{Nitrous acid.}}{\left(\left.\begin{matrix}NO \\ H\end{matrix}\right\} O\right)} = \underset{\text{Nitrogen.}}{\left.\begin{matrix}N \\ N\end{matrix}\right\}}$$

$$+ \underset{\text{Water.}}{\left(\left.\begin{matrix}H \\ H\end{matrix}\right\} O\right)} + \underset{\text{Lactic acid.}}{\left(C^3H^4O''\left\{\begin{matrix}OH \\ OH\end{matrix}\right.\right)}$$

3rd. Lactic acid is also produced when chloropropionic acid is heated with moist oxide of silver:

$$2\underset{\text{Chloropropionic acid.}}{\left(\left.\begin{matrix}C^3H^4ClO \\ H\end{matrix}\right\} O\right)} + \underset{\text{Oxide of silver.}}{\left(\left.\begin{matrix}Ag \\ Ag\end{matrix}\right\} O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H \\ H\end{matrix}\right\} O\right)} = 2\underset{\text{Chloride of silver.}}{\left(\left.\begin{matrix}Ag \\ Cl\end{matrix}\right\}\right)}$$

$$+ 2\underset{\text{Lactic acid.}}{\left(C^3H^4O''\left\{\begin{matrix}OH \\ OH\end{matrix}\right.\right)}$$

4th. Wurtz has succeeded in preparing lactic acid by the oxidation of propyl-glycol:

$$\underset{\text{Propyl-glycol.}}{\left(C^3H^{6''}\left\{\begin{matrix}OH \\ OH\end{matrix}\right.\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O \\ O\end{matrix}\right\}} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H \\ H\end{matrix}\right\} O\right)} + \underset{\text{Lactic acid.}}{\left(C^3H^4O''\left\{\begin{matrix}OH \\ OH\end{matrix}\right.\right)}$$

5th. Wislicenus has obtained lactic acid by heating cyanhydrin of glycol with an alcoholic solution of potash. This cyanhydrin was prepared by the reaction of cyanide of potassium in alcoholic solution on chlorhydrin:

$$\underset{\text{Cyanhydrin of ethyl-glycol.}}{\left(C^2H^{4''}\left\{\begin{matrix}OH \\ CN\end{matrix}\right.\right)} + \underset{\text{Hydrate of potassium.}}{\left(\left.\begin{matrix}K \\ H\end{matrix}\right\} O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H \\ H\end{matrix}\right\} O\right)} = \underset{\text{Ammonia.}}{\left(\left.\begin{matrix}H \\ H \\ H\end{matrix}\right\} N\right)}$$

$$+ \underset{\text{Lactate of potassium.}}{\left(C^2H^{4''}\left\{\begin{matrix}OH \\ C\left\{\begin{matrix}O'' \\ OK\end{matrix}\right.\end{matrix}\right.\right)}$$

This process gives, not the lactic acid of fermentation, but the sarkolactic acid.

6th. Lippemann has prepared the chloride of lactyl $\left(C^3H^4O''\left\{\begin{matrix}Cl \\ Cl\end{matrix}\right.\right)$ synthetically by causing the oxychloride of carbon to act on ethylene:

$$\underset{\text{Ethylene.}}{\left(C^2H^4\right)} + \underset{\text{Oxychloride of carbon.}}{\left(CO''\left\{\begin{matrix}Cl \\ Cl\end{matrix}\right.\right)} = \underset{\text{Chloride of lactyl.}}{\left(C^3H^4O''\left\{\begin{matrix}Cl \\ Cl\end{matrix}\right.\right)}$$

PROPERTIES.—Lactic acid is a colourless, inodorous, syrupy liquid, the density of which is 1·215 at 20°·5. It has a very acid taste, absorbs moisture readily, and is soluble in water and alcohol in all proportions; it is less soluble in ether, and remains fluid at −24°. It coagulates albumen, and two drops added to 100 grammes of milk will cause its immediate coagulation.

Lactic acid does not affect the aqueous solutions of lime, baryta, or strontia; it sets acetic acid free, when boiled with the acetates, and dissolves the phosphate of calcium from bones.

The acetates of zinc and magnesium in aqueous solution are decomposed by lactic acid: lactate of zinc or of magnesium is deposited, and acetic acid is set free. On the contrary, the lactate of zinc is decomposed by the acetate of potassium with the formation of potassic lactate and acetate of zinc.

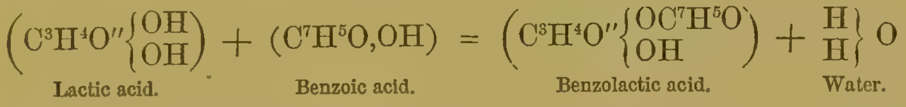
The aqueous solution of lactate of copper becomes blue on the addition of potash: hydrate of calcium precipitates all the copper contained in this alkaline solution in the state of hydrate.

When lactic acid is heated with concentrated sulphuric acid, pure oxide of carbon is disengaged, and the mixture becomes brown.

Heated with a mixture of binoxide of manganese, salt, and sulphuric acid, lactic acid furnishes chloral and aldehyd; when only a small quantity of chlorine is disengaged, it is aldehyd which is chiefly formed.

Boiling nitric acid transforms lactic into oxalic acid.

When a mixture of 10 parts of lactic and 14 parts of benzoic acids are heated for several hours at 200°, water is disengaged, and a new acid—the benzolactic—is formed:

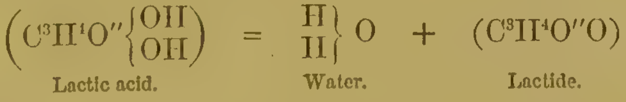


$$\underset{\text{Lactic acid.}}{\left(C^3H^4O''\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)} + \underset{\text{Benzoic acid.}}{(C^7H^5O,OH)} = \underset{\text{Benzolactic acid.}}{\left(C^3H^4O''\left\{\begin{matrix}OC^7H^5O\\OH\end{matrix}\right.\right)} + \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O}$$

In order to separate this acid from the excess of benzoic acid, it is dissolved with an insufficient quantity of sodic carbonate, which then dissolves it alone. The liquid is agitated with ether to eliminate the free benzoic acid which the water has dissolved, and then hydrochloric acid is added. The benzolactic acid is deposited in crystals.

This acid is the homologue of the benzoglycolic acid which is produced when hippuric acid is acted upon by nitrous vapours.

When syrupy lactic acid is submitted to a temperature of 140°, very dilute lactic acid first distils; if the operation be discontinued when all distillation has ceased, the residue crystallizes on cooling. These crystals constitute lactide or lactic anhydride ($C^3H^4O''O$):



$$\underset{\text{Lactic acid.}}{\left(C^3H^4O''\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)} = \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O} + \underset{\text{Lactide.}}{(C^3H^4O''O)}$$

When strongly heated, lactide distils, and is partially decomposed. Among the products of its decomposition are found aldehyd, citraconic acid, carbonic anhydride, and oxide of carbon:

$$\underset{\text{Lactide.}}{(C^3H^4O''O)} = \underset{\text{Oxide of carbon.}}{CO} + \underset{\text{Aldehyd.}}{(C^2H^4O)}$$

$$\underset{\text{Lactic acid.}}{4\left(C^3H^4O''\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)} = \underset{\text{Citraconic acid.}}{(C^5H^6O^4)} + \underset{\text{Aldehyd.}}{3(C^2H^4O)} + \underset{\text{Carbonic anhydride.}}{CO^2} + \underset{\text{Water.}}{3(H^2O)}$$

If the action of heat on lactic acid be less prolonged, instead of lactide, dilactic acid ($C^6H^{10}O^5$) will be obtained:

$$\underset{\text{Lactic acid.}}{2\left(C^3H^4O''\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)} = \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O} + \underset{\text{Dilactic acid.}}{\left(\begin{matrix}C^3H^4O''\left\{\begin{matrix}OH\\O''\end{matrix}\right.\\C^3H^4O''\left\}\begin{matrix}OH\end{matrix}\right.\end{matrix}\right)}$$

Though biatomic, lactic acid is monobasic. It only exchanges one atom of hydrogen for metals. Thus the neutral lactates have the formula $\left(C^3H^4O''\left\{\begin{matrix}OH\\OM'\end{matrix}\right.\right)$.

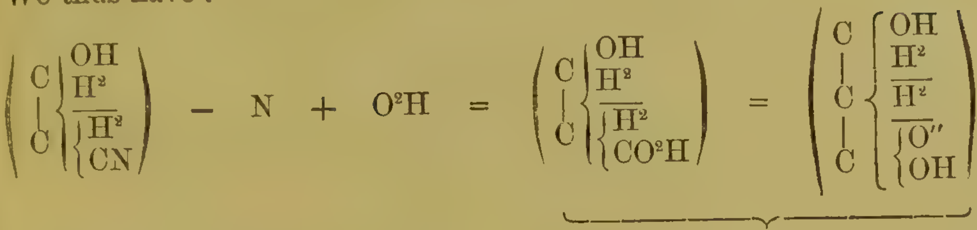
All the lactates are insoluble in ether, readily soluble in boiling water, but scarcely soluble in cold water or alcohol. The alkaline lactates are exceptions to this rule; they readily dissolve in cold water.

The isomerism of the lactic acid of fermentation with sarkolactic acid is especially apparent in their salts. Thus the ferrous lactate is crystallizable and retains three molecules of water, while ferrous sarkolactate is not crystallizable.

It would be repetition to speak here of the numerous reactions which establish the biatomic and monobasic character of lactic acid. We have already treated this question completely when speaking of biatomic and monobasic acids in general, and lactic acid, the best known of these, was continually given as an example.

Sarkolactic acid is obtained, as has been said, by the action of oxychloride of carbon on ethylene $\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^2\\\overline{H^2}\end{matrix}\right.\right)$, and by the action of potash on the cyanhydrin of glycol $\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}OH\\H^2\\\overline{H^2}\\CN\end{matrix}\right.\right)$. On the contrary, true lactic acid is produced when aldehyd reacts on hydrocyanic acid and water. According to these syntheses, the formula of constitution of sarkolactic acid is $\left(\begin{matrix}C\\|\\C\\|\\C\end{matrix}\left\{\begin{matrix}OH\\H^2\\\overline{H^2}\\\overline{O''}\\OH\end{matrix}\right.\right)$, and that of true lactic acid is $\left(\begin{matrix}C\\|\\C\\|\\C\end{matrix}\left\{\begin{matrix}H^3\\\overline{H}\\OH\\\overline{O''}\\OH\end{matrix}\right.\right)$.

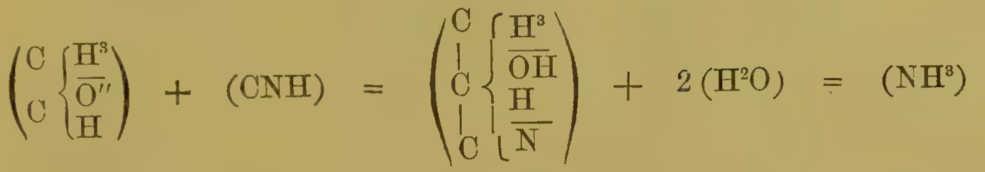
We thus have :



$$\left(\begin{matrix}C\\|\\C\end{matrix}\left\{\begin{matrix}OH\\H^2\\\overline{H^2}\\CN\end{matrix}\right.\right) - N + O^2H = \underbrace{\left(\begin{matrix}C\\|\\C\end{matrix}\left\{\begin{matrix}OH\\H^2\\\overline{H^2}\\CO^2H\end{matrix}\right.\right) = \left(\begin{matrix}C\\|\\C\\|\\C\end{matrix}\left\{\begin{matrix}OH\\H^2\\\overline{H^2}\\\overline{O''}\\OH\end{matrix}\right.\right)}$$

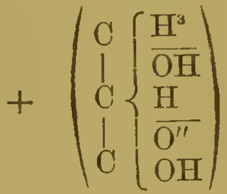
Cyanhydrin of glycol. Nitrogen. Water. Sarkolactic acid.

and



$$\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\\overline{O''}\\H\end{matrix}\right.\right) + (CNH) = \left(\begin{matrix}C\\|\\C\\|\\C\end{matrix}\left\{\begin{matrix}H^3\\\overline{OH}\\H\\\overline{N}\end{matrix}\right.\right) + 2\,(H^2O) = (NH^3)$$

Aldehyd. Hydrocyanic acid. An unknown intermediate body. Water. Ammonia.

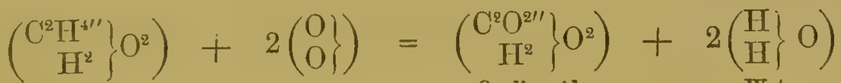


$$+\left(\begin{matrix}C\\|\\C\\|\\C\end{matrix}\left\{\begin{matrix}H^3\\\overline{OH}\\H\\\overline{O''}\\OH\end{matrix}\right.\right)$$

Normal lactic acid.

## BIATOMIC AND BIBASIC ACIDS.

PREPARATION.—*First Process.*—These acids may be obtained by the oxidation of the corresponding glycols :



$$\left(\left.\begin{matrix}C^2H^{4''}\\H^2\end{matrix}\right\}O^2\right) + 2\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\right) = \left(\left.\begin{matrix}C^2O^{2''}\\H^2\end{matrix}\right\}O^2\right) + 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

Glycol. Oxygen. Oxalic acid. Water.

But this oxidation has only succeeded with ordinary glycol. It is true that propyl-glycol appears to have given malonic acid $\left(\left.\begin{matrix}C^3H^2O^{2''}\\H^2\end{matrix}\right\}O^2\right)$, but in the oxidation of butyl and amyl-glycol, no acid homologous with the preceding has been obtained. Perhaps this might be accomplished by operating on larger quantities. The slight stability of the complicated molecules, which are entirely separated when the attempt is made to oxidize them, has hitherto prevented the operation being successful.

*Second Process.* — Bicyanides of biatomic alcohol radicles are boiled with a concentrated alcoholic solution of potash; ammonia is disengaged, and there remains in solution the alkaline salt of an acid which corresponds to the glycol higher by two terms than that whose bicyanhydrin has been employed.

Thus the bicyanhydrin of glycol $C^2H^6O^2$ gives succinic acid, $C^4H^6O^4$, corresponding to butyl-glycol, $C^4H^{10}O^2$, which constitutes the second higher homologue of ordinary glycol.

The reaction which gives rise to the formation of these acids by means of the hydrocyanic ethers and potash is expressed by the following equation, or by an analogous one:

$$\underset{\text{Cyanide of propylene.}}{\left(C^3H^{6\prime\prime}\left\{\begin{matrix}CN\\CN\end{matrix}\right.\right)} + \underset{\text{Potash.}}{2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Pyrotartrate of potassium.}}{\left(C^3H^{6\prime\prime}\left\{\begin{matrix}CO^2K\\CO^2K\end{matrix}\right.\right)}$$

$$+ \underset{\text{Ammonia.}}{2\left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right)}$$

The cyanides used in these processes should be prepared by heating the bromides of the same radicles with a solution of cyanide of potassium in dilute alcohol:

$$\underset{\text{Bromide of ethylene.}}{\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\Br^2\end{matrix}\right\}\right)} + \underset{\text{Potassic cyanide.}}{2\left(\left.\begin{matrix}K\\CN\end{matrix}\right\}\right)} = \underset{\text{Potassic bromide.}}{2\left(\left.\begin{matrix}K\\Br\end{matrix}\right\}\right)} + \underset{\text{Cyanide of ethylene.}}{\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\(CN)^2\end{matrix}\right\}\right)}$$

It is not necessary to purify the bicyanhydrins used in the preparation of these acids.

The acids obtained by this process appear so far to be entirely identical with those obtained by other methods.

*Third Process.*—Several of these acids may be obtained by fixing hydrogen on other less hydrogenized acids; thus itaconic acid and its isomers, citraconic and mesaconic acids, can fix $H^2$ and be converted into pyrotartaric acid.

It is the same with maleic and fumaric acids, which, by fixing $H^2$, give succinic acid:

$$\underset{\text{Fumaric acid.}}{(C^4H^4O^4)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}} = \underset{\text{Succinic acid.}}{(C^4H^6O^4)}$$

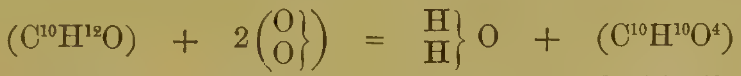
$$\underset{\text{Itaconic acid.}}{(C^5H^6O^4)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}} = \underset{\text{Pyrotartaric acid.}}{(C^5H^8O^4)}$$

*Fourth Process.*—Acids of this group are also formed by the action of heat on other more complicated acids. Thus, on causing heat to act on tartaric acid, pyrotartaric acid is formed:

$$\underset{\text{Tartaric acid.}}{2\,(C^4H^6O^6)} = \underset{\text{Pyrotartaric acid.}}{(C^5H^8O^4)} + \underset{\text{Carbonic anhydride.}}{3\,(CO^2)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

*Fifth Process.*—Many of these acids are obtained by heating different substances with a powerful oxidizer. Sometimes these reactions are sufficiently clear, but occasionally they are very complicated.

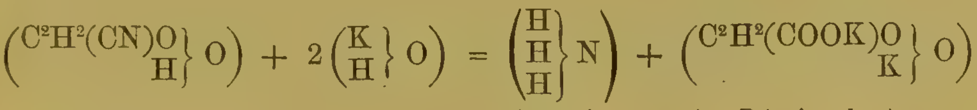
For instance, if cuminic aldehyd be strongly oxidized, insolinic acid is formed :



$$\underset{\text{Cuminic acid.}}{(C^{10}H^{12}O)} + \underset{\text{Oxygen.}}{2\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\right)} = \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O} + \underset{\text{Insolinic acid.}}{(C^{10}H^{10}O^4)}$$

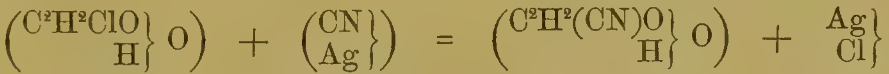
On the contrary, if nitric acid be made to react on fatty substances, succinic acid and several of its homologues are obtained. The molecule of the fatty substance is entirely destroyed, and no simple relation is observed between the generating bodies and their derivatives.

*Sixth Process.*—Kolbe and Hugo Müller have each obtained one of these acids, malonic acid, by heating aceto-cyanic acid with caustic potash :



$$\underset{\text{Aceto-cyanic acid.}}{\left(\left.\begin{matrix}C^2H^2(CN)O\\H\end{matrix}\right\}O\right)} + \underset{\text{Potash.}}{2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Ammonia.}}{\left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right)} + \underset{\text{Potassic malonate.}}{\left(\left.\begin{matrix}C^2H^2(COOK)O\\K\end{matrix}\right\}O\right)}$$

The aceto-cyanic acid used for this synthesis is prepared by heating chloracetic acid with cyanide of silver in a hermetically-sealed tube :

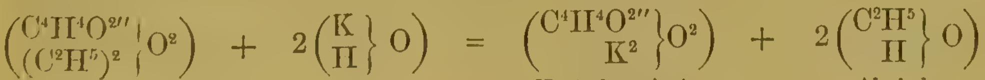


$$\underset{\text{Chloracetic acid.}}{\left(\left.\begin{matrix}C^2H^2ClO\\H\end{matrix}\right\}O\right)} + \underset{\text{Cyanide of silver.}}{\left(\left.\begin{matrix}CN\\Ag\end{matrix}\right\}\right)} = \underset{\text{Aceto-cyanic acid.}}{\left(\left.\begin{matrix}C^2H^2(CN)O\\H\end{matrix}\right\}O\right)} + \underset{\text{Chloride of silver.}}{\left.\begin{matrix}Ag\\Cl\end{matrix}\right\}}$$

Properties.—It will be supposed that in this group of acids, as in all the others, both saturated and non-saturated bodies are to be found. These present different characters, and we will therefore consider them separately.

**Saturated Acids.**—1st. These acids, being bibasic, have two atoms of typical hydrogen, which may both be replaced by positive metals. They can form two classes of salts : acid salts, resulting from the substitution of a metallic radicle for one atom of hydrogen, and neutral salts, resulting from the replacement of the two atoms of hydrogen by two equivalents of metal.

2nd. Ethers having two alcohol radicles are obtained by processes described elsewhere for the preparation of compound ethers. When these ethers are submitted to the action of alkalies, they are completely saponified. Two molecules of alcohol are produced, and a neutral salt of the acid of which the ether contained the elements :



$$\underset{\text{Neutral succinate of ethyl.}}{\left(\left.\begin{matrix}C^4H^4O^{2\prime\prime}\\(C^2H^5)^2\end{matrix}\right\}O^2\right)} + \underset{\text{Potash.}}{2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Neutral succinate of potassium.}}{\left(\left.\begin{matrix}C^4H^4O^{2\prime\prime}\\K^2\end{matrix}\right\}O^2\right)} + \underset{\text{Alcohol.}}{2\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)}$$

However, if these ethers be saponified by half the quantity of potash required for complete saponification, a single atom of ethyl is eliminated in the state of alcohol, and there is then produced a potassic salt of an acid ether from which this ether itself can be obtained :

$$\left(\left.\begin{matrix} C^4H^4O^{2\prime\prime} \\ (C^2H^5)^2 \end{matrix}\right\} O^2\right) + \left.\begin{matrix} K \\ H \end{matrix}\right\} O = \left(\left.\begin{matrix} C^2H^5 \\ H \end{matrix}\right\} O\right) + \left(\left.\begin{matrix} C^4H^4O^{2\prime\prime} \\ C^2H^5 \\ K \end{matrix}\right\} O^2\right)$$

Neutral succinate of ethyl. Potash. Alcohol. Ethyl-succinate of potassium.

These acids therefore form two ethers : one containing two alcohol radicles, the other only one : but it must be remarked that, contrary to what is the case with monobasic and biatomic acids, there is only produced here a single mono-alcoholic ether, which is always acid. This is owing to the fact, that here the two atoms of typical hydrogen have the same properties, while in monobasic and biatomic acids these properties are different.

3rd. When submitted to the action of heat, they are capable of losing the elements of water and furnishing anhydrides :

$$(C^4H^6O^4) = (C^4H^4O^3) + H^2O$$

Succinic acid. Succinic anhydride. Water.

These anhydrides can again unite with water, and reconstitute the acids whence they are derived.

4th. These acids give either monatomic or biatomic residues, on losing the group OH once or twice :

$$\left(\left.\begin{matrix} R'' \\ H^2 \end{matrix}\right\} O^2\right) - HO = \left(\left.\begin{matrix} R'' \\ H \end{matrix}\right\} O\right)'$$

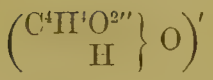
$$\left.\begin{matrix} R'' \\ H^2 \end{matrix}\right\} O^2 - 2\,(HO) = R''$$

The first of these radicles may be substituted for hydrogen in ammonia, and the compound resulting from this substitution $\left.\begin{matrix} \left(\left.\begin{matrix} R'' \\ H \end{matrix}\right\} O\right)' \\ H^2 \end{matrix}\right\} N$, is acid. It is not probable that a neutral isomer of this body exists. As the two atoms of typical hydrogen are positive in this class of acids, whichever may be the one removed that which remains is, of course, still positive.

The biatomic radicle R″ may be substituted for $H^2$ in the simple ammonia type ; thence the bodies which take the name of imides $\left(\left.\begin{matrix} R'' \\ H \end{matrix}\right\} N\right)$; but it may also be substituted for $H^2$ in the type $N^2H^6$. It then gives a neutral diamide $\left(\left.\begin{matrix} R'' \\ H^4 \end{matrix}\right\} N^2\right)$

$$\text{Ex.} \quad \left(\left.\begin{matrix} C^4H^4O^{2\prime\prime} \\ H^2 \end{matrix}\right\} O^2\right)$$

Succinic acid.

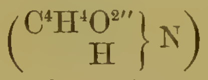


$$\left(\left.\begin{matrix}C^4H^4O^{2\prime\prime}\\ H\end{matrix}\right\}O\right)^{\prime}$$

Monatomic residue of succinic acid.

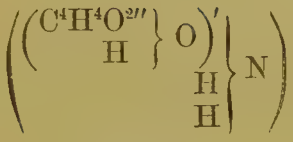
$C^4H^4O^{2\prime\prime}$

Biatomic radicle of succinic acid.



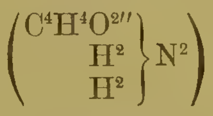
$$\left(\left.\begin{matrix}C^4H^4O^{2\prime\prime}\\ H\end{matrix}\right\}N\right)$$

Succinimide.



$$\left(\left.\begin{matrix}\left(\left.\begin{matrix}C^4H^4O^{2\prime\prime}\\ H\end{matrix}\right\}O\right)^{\prime}\\ H\\ H\end{matrix}\right\}N\right)$$

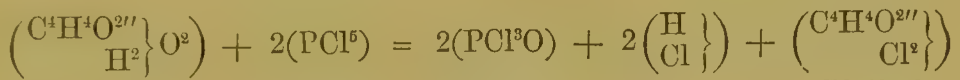
Succinamic acid.



$$\left(\left.\begin{matrix}C^4H^4O^{2\prime\prime}\\ H^2\\ H^2\end{matrix}\right\}N^2\right)$$

Succinic diamide (succinamide).

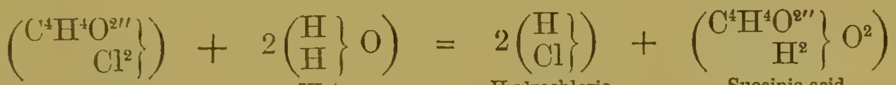
5th. Perchloride of phosphorus transforms the acids of this group into chlorides of their radicles:



$$\left(\left.\begin{matrix}C^4H^4O^{2\prime\prime}\\ H^2\end{matrix}\right\}O^2\right) + 2(PCl^5) = 2(PCl^3O) + 2\left(\left.\begin{matrix}H\\ Cl\end{matrix}\right\}\right) + \left(\left.\begin{matrix}C^4H^4O^{2\prime\prime}\\ Cl^2\end{matrix}\right\}\right)$$

Succinic acid. Perchloride of phosphorus. Oxychloride of phosphorus. Hydrochloric acid. Chloride of succinyl.

These chlorides may be entirely decomposed by water, and re-form their respective acids:



$$\left(\left.\begin{matrix}C^4H^4O^{2\prime\prime}\\ Cl^2\end{matrix}\right\}\right) + 2\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right) = 2\left(\left.\begin{matrix}H\\ Cl\end{matrix}\right\}\right) + \left(\left.\begin{matrix}C^4H^4O^{2\prime\prime}\\ H^2\end{matrix}\right\}O^2\right)$$

Chloride of succinyl. Water. Hydrochloric acid. Succinic acid.

6th. Distilled with an excess of base, these acids lose two molecules of carbonic anhydride, and thereby each gives rise to the fundamental hydrocarbide of the series two terms lower than that of the acid whence it arises. Thus adipic acid ($C^6H^{10}O^4$), which belongs to the hexylic series, gives hydride of butyl ($C^4H^{10}$), the fundamental hydrocarbide of the butylic series. This series is lower by two terms than the hexylic series, of which the term corresponding to hydride of butyl, the hydride of hexyl $C^6H^{14}$, contains twice $CH^2$ more:

$$(C^6H^{10}O^4) = 2(CO^2) + (C^4H^{10})$$

Adipic acid. Carbonic anhydride. Hydride of butyl.

It will be observed that on distilling the acids of this group with an excess of base, we descend two terms in the homologous series, while we only descend one term when monatomic acids are submitted to similar treatment.

7th. Bromine acts on these acids when heated with them. The monobrominated and bibrominated derivatives may be easily obtained by operating in hermetically-sealed tubes. Boiled with oxide of silver and water, the brominated products lose all their bromine in the state of bromide of silver, the group HO being substituted for each molecule of bromine. New acids result, which differ from those whence they arise by one or two atoms of oxygen more, and consequently their atomicity is greater:

$$\underset{\text{Monobromo-succinic acid.}}{2(C^4H^5BrO^4)} + \underset{\text{Oxide of silver.}}{(Ag^2O)} + \underset{\text{Water.}}{(H^2O)} = \underset{\text{Bromide of silver.}}{2(AgBr)} + \underset{\text{Malic acid.}}{2(C^4H^6O^5)}$$

$$\underset{\text{Bibromo-succinic acid.}}{(C^4H^4Br^2O^4)} + \underset{\text{Oxide of silver.}}{Ag^2O} + \underset{\text{Water.}}{H^2O} = \underset{\text{Bromide of silver.}}{2(AgBr)} + \underset{\text{Tartaric acid.}}{(C^4H^6O^6)}$$

Malic and tartaric acids differ from succinic acid; the first by one and the second by two atoms of oxygen. Their atomicity is greater than that of succinic acid.

8th. Treated with baryta, bibrominated acids can lose a molecule of hydrobromic acid and be transformed into non-saturated monobrominated acids:

$$\underset{\text{Bibromo-succinic acid.}}{2(C^4H^4Br^2O^4)} + \underset{\text{Baryta.}}{(Ba''O)} = \underset{\text{Bromide of barium.}}{(Ba''Br^2)} + \underset{\text{Water.}}{H^2O} + \underset{\text{Bromo-maleic acid.}}{2(C^4H^3BrO^4)}$$

If the alkali be in excess, two molecules of hydrobromic acid may be separated:

$$\underset{\text{Bibromo-pyrotartaric acid.}}{\left(C^5H^6Br^2O^4\right)} + \underset{\text{Soda.}}{2\left(\left.\begin{matrix}Na\\H\end{matrix}\right\}O\right)} = \underset{\text{Bromide of sodium.}}{2\left(\left.\begin{matrix}Na\\Br\end{matrix}\right\}\right)}$$

$$+ \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Aconic acid.}}{\left(C^5H^4O^4\right)}$$

**Non-saturated Acids.**—1st. While the formulæ of the saturated acids of this group belong each to a single acid, those of the non-saturated acids each belong to several isomers. Thus, the formula $(C^4H^6O^4)$ only belongs to succinic acid; but the formula $(C^4H^4O^4)$ belongs to two different bodies, maleic and fumaric acids. So also to pyrotartaric acid $(C^5H^8O^4)$, no isomer of which is known, there correspond three non-saturated acids all having the formula $(C^5H^6O^4)$: these are itaconic, citraconic, and mesaconic acids.

2nd. Like the saturated, the non-saturated acids give an anhydride by the action of heat, and a bichloride under the influence of pentachloride of phosphorus. It is not known whether they can be made to produce a carburetted hydrogen by distillation with an excess of base.

3rd. Submitted to the action of nascent hydrogen, they absorb sufficient to pass to the state of saturated acids:

$$\underset{\text{Itaconic acid.}}{\left(C^5H^6O^4\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}} = \underset{\text{Pyrotartaric acid.}}{\left(C^5H^8O^4\right)}$$

In this case the different non-saturated isomers give the same saturated product: pyrotartaric acid possesses the same properties, whether it arises from the hydrogenation of itaconic, citraconic, or of mesaconic acid.

4th. Bromine combines directly with non-saturated acids, giving bibrominated derivatives of saturated acids. Thus, fumaric acid is transformed into bibromo-succinic acid:

$$\underset{\text{Fumaric acid.}}{(C^4H^4O^4)} \quad + \quad \underset{\text{Bromine.}}{Br^2} \quad = \quad \underset{\text{Bibromo-succinic acid.}}{(C^4H^4Br^2O^4)}$$

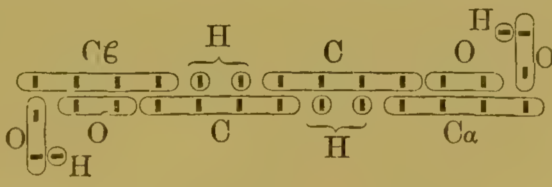
It must however be remarked that, while the fixation of hydrogen reduces non-saturated isomers into an identical product, the fixation of bromine gives rise to the formation of brominated products isomeric among themselves, like the acids which gave rise to them. When hydrogen is substituted for the bromine of these different isomeric brominated compounds, we again return to the single saturated acid.

5th. These acids unite also with hydrobromic acid, forming monobrominated derivatives of the corresponding saturated bodies. It is probable that in this case the isomerism remains:

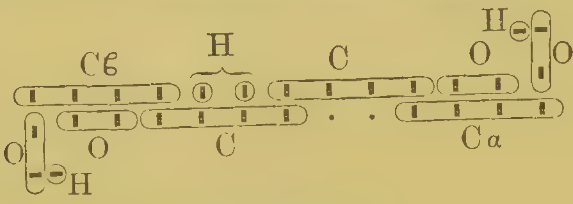
$$\underset{\text{Fumaric acid.}}{(C^4H^4O^4} \quad + \quad \underset{\text{Hydrobromic acid.}}{(HBr)} \quad = \quad \underset{\text{Monobromo-succinic acid.}}{(C^4H^5BrO^4)}$$

Kékulé, who discovered these facts, gives the following explanation of them:

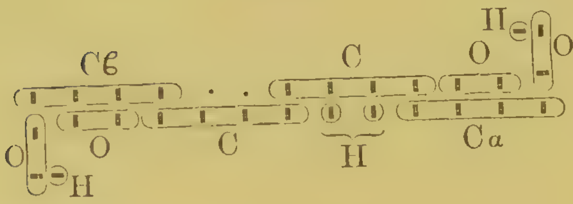
Succinic acid, which we will take as example, contains two atoms of hydrogen, both of them typical and basic. It may be considered as containing four atoms of carbon in juxtaposition, the two external of which retain three-fourths, and the two centre ones only half of their capacity for saturation. The following figure indicates this constitution:



Kékulé supposes that, in the two external atoms of carbon Cα and Cϵ, one atomicity is saturated by oxygen O, the second centre of attraction of which is united to hydrogen H. This hydrogen, united to the carbon by means of the oxygen, is typical. Moreover, Kékulé supposes that the two atomicities which remain in the two external atoms of carbon are saturated by oxygen, the vicinity of which gives basic properties to the hydrogen. There remain the two intermediate atoms of carbon, which have each two atomicities saturated by hydrogen. If one of these two atoms of carbon were to lose the two atoms of hydrogen to which it is united, we should have a non-saturated acid, which could combine directly with hydrogen or any other monatomic body. The form of the molecule will be different, according to whether it be one or the other of the two atoms of carbon which has lost its hydrogen, and, consequently, we may have two isomeric acids, as the two following figures represent:

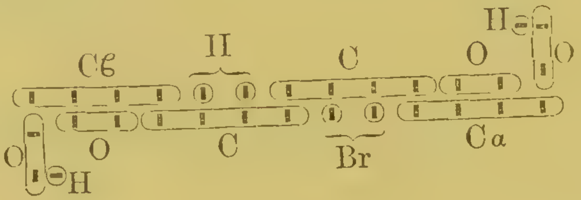


and

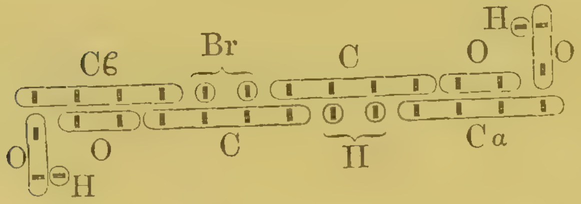


It will be seen by these figures that it is sometimes at the cost of the one, and sometimes at that of the other of the two middle atoms of carbon, that the elimination of the hydrogen is effected.

If hydrogen be added to the non-saturated body, in both cases the molecule assumes the single form assigned to the saturated acid. On the contrary, if bromine be added, it takes the place of the absent hydrogen, and consequently occupies different positions, according as the gap left by the disappearance of the hydrogen is at the one point or the other. There are therefore two isomeric brominated acids, as the following figures indicate:



and



According to this hypothesis of Kékulé, therefore, the number of isomers possible depends on the number of atoms of carbon intermediate between the two external atoms. To succinic acid, which contains two, there should correspond two bibrominated derivatives and two non-saturated bodies; to pyrotartaric acid, which contains three, there should correspond three; and, in general, to any acid there should correspond a number of these equal to $n-2$, $n$ being the number of atoms of carbon it contains.

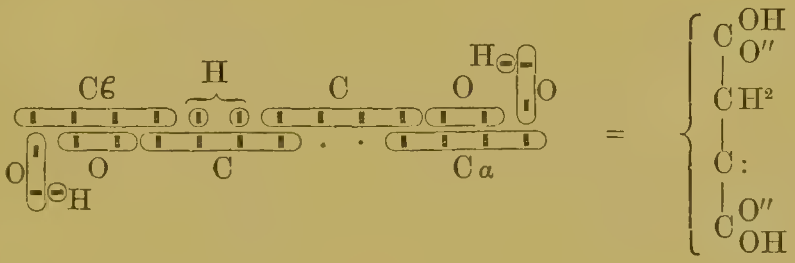
The theory is verified in the two cases hitherto observed. Two non-saturated isomers correspond to succinic acid and three to pyrotartaric acid.

This hypothesis is correctly based: the isomerism of the acids in question is owing to the place left vacant by the hydrogen; but we believe that Kékulé is mistaken in his attempt to determine this place. We think the formulæ he gives are not those of isomeric but of identical acids. All being symmetrical in the formula of succinic acid, and each internal atom being equally near ($CO^2H$), it is of little consequence whether the hydrogen have been eliminated at the cost of one or the other.

But there is another mode of isomerism possible, that which causes the isomerism of oxide of ethylene and aldehyd: the hydrogen may be eliminated at the cost of a single atom or of two atoms of carbon.

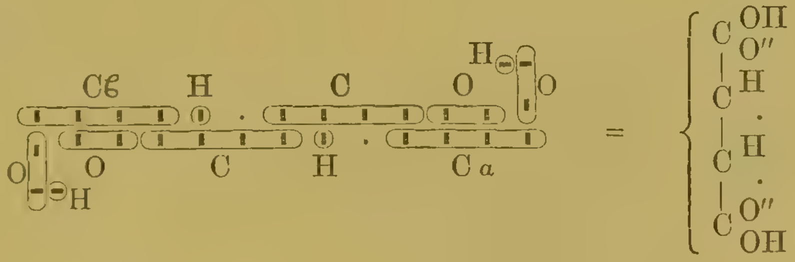
Hence the possibility of two acids $C^4H^4O^4$:

1st.



$$\left\{\begin{array}{l} \mathrm{C}^{\mathrm{OH}}_{\mathrm{O''}} \\ | \\ \mathrm{CH^2} \\ | \\ \mathrm{C}: \\ | \\ \mathrm{C}^{\mathrm{O''}}_{\mathrm{OH}} \end{array}\right.$$

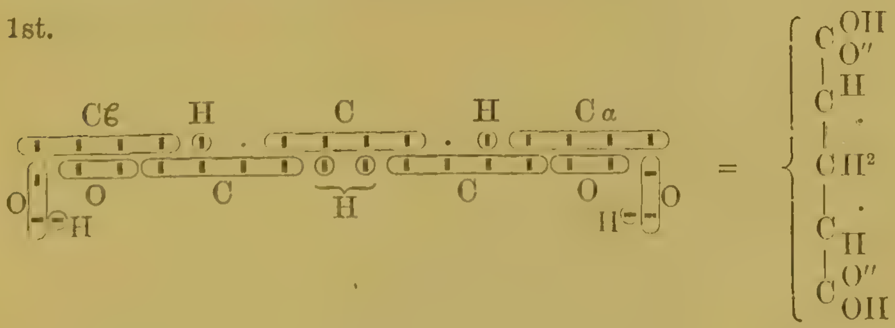
2nd.



$$\left\{\begin{array}{l} \mathrm{C}^{\mathrm{OH}}_{\mathrm{O''}} \\ | \\ \mathrm{C}^{\mathrm{H}}\,. \\ | \\ \mathrm{C}^{\mathrm{H}}\,. \\ | \\ \mathrm{C}^{\mathrm{O''}}_{\mathrm{OH}} \end{array}\right.$$

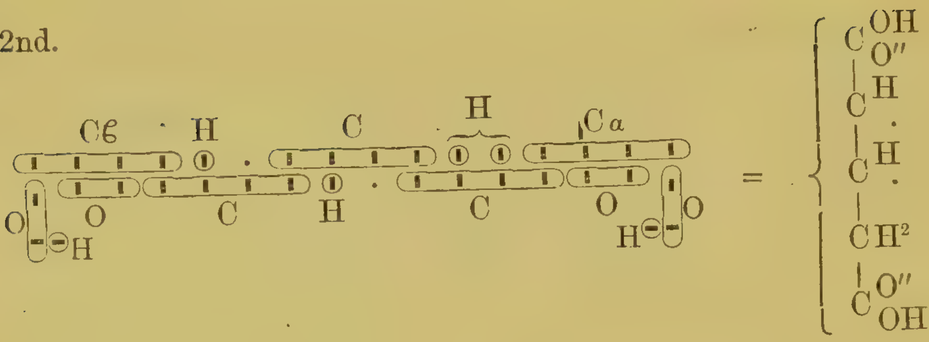
and of four acids answering to the formula $C^5H^6O^4$:

1st.



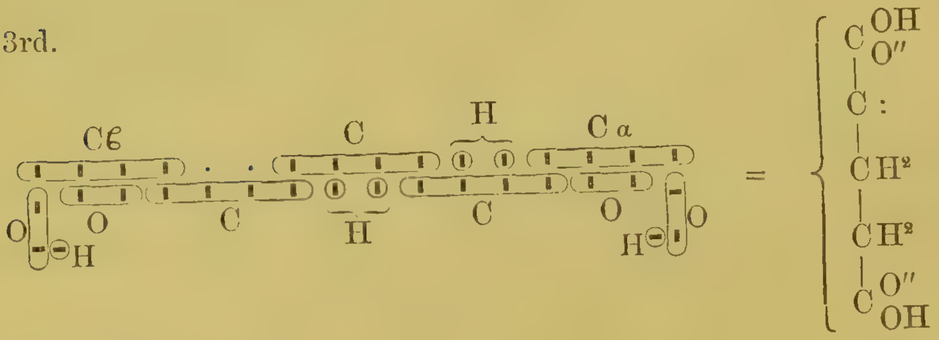
$$\left\{\begin{array}{l} \mathrm{C}^{\mathrm{OH}}_{\mathrm{O''}} \\ | \\ \mathrm{C}^{\mathrm{H}}\,. \\ | \\ \mathrm{CH^2} \\ |\;. \\ \mathrm{C}^{\mathrm{H}} \\ | \\ \mathrm{C}^{\mathrm{O''}}_{\mathrm{OH}} \end{array}\right.$$

2nd.



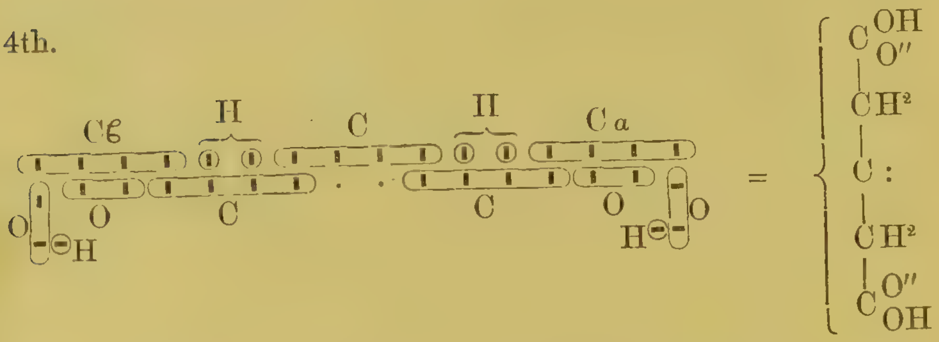
$$= \left\{ \begin{array}{l} C\begin{matrix}OH\\O''\end{matrix} \\ | \\ C\,H\,. \\ | \\ C\,H\,. \\ | \\ CH^2 \\ | \\ C\begin{matrix}O''\\OH\end{matrix} \end{array} \right.$$

3rd.



$$= \left\{ \begin{array}{l} C\begin{matrix}OH\\O''\end{matrix} \\ | \\ C\,: \\ | \\ CH^2 \\ | \\ CH^2 \\ | \\ C\begin{matrix}O''\\OH\end{matrix} \end{array} \right.$$

4th.



$$= \left\{ \begin{array}{l} C\begin{matrix}OH\\O''\end{matrix} \\ | \\ CH^2 \\ | \\ C\,: \\ | \\ CH^2 \\ | \\ C\begin{matrix}O''\\OH\end{matrix} \end{array} \right.$$

The modification we propose in M. Kékulé's theory, supposes a fourth isomer of itaconic, citraconic, and mesaconic acids.

**Condensed Acids.**—The biatomic radicles of this group ought, like all the others, to have the property of accumulating in the molecules, giving products of condensation. These products have, however, been little studied. As yet, disuccinic acid, described by Schiff, is the only condensed acid of this group known. According to this chemist, it is formed when succinic acid is carefully heated, so as not to produce complete dehydration:

$$\underset{\text{Succinic acid.}}{2\left(C^4H^4O^{2''}\begin{Bmatrix}OH\\OH\end{Bmatrix}\right)} = \underset{\text{Water.}}{\left(\begin{matrix}H\\H\end{matrix}\Big\}\,O\right)} + \underset{\text{Disuccinic acid.}}{\left(\begin{matrix}C^4H^4O^{2''}\\C^4H^4O^{2''}\end{matrix}\begin{Bmatrix}OH\\O''\\OH\end{Bmatrix}\right)}$$

**Acids of this Group which are actually known.** — SATURATED ACIDS:

1st. *In the series* $C^nH^{2n-2}O^4$:

Oxalic acid $C^2H^2O^4$, corresponding to the glycol $C^2H^6O^2$.

Malonic acid $C^3H^4O^4$, corresponding to propyl-glycol $C^5H^8O^2$.

Succinc acid $C^4H^6O^4$, corresponding to butyl-glycol $C^4H^{10}O^2$.
Pyrotartaric acid $C^5H^8O^4$, corresponding to amyl-glycol $C^5H^{12}O^2$.
Adipic acid $C^6H^{10}O^4$, corresponding to hexyl-glycol $C^6H^{14}O^2$.
Pimelic acid $C^7H^{12}O^4$, corresponding to heptyl-glycol $C^7H^{16}O^2$*.
Suberic acid $C^8H^{14}O^4$, corresponding to octyl-glycol $C^8H^{18}O^2$.
Sebacic acid $C^{10}H^{18}O^4$, corresponding to decyl-glycol $C^{10}H^{22}O^2$*.

2nd. *In the series* $C^nH^{2n-8}O^4$:

Quinonic acid $C^6H^4O^4$, corresponding to the unknown glycol $C^6H^8O^2$*.

3rd. *In the series* $C^nH^{2n-10}O^4$:

Phthalic acid $C^8H^6O^4$, and its isomer terephthalic acid, corresponding to tollyl-glycol $C^8H^{10}O^2$.*

An unnamed acid $C^9H^8O^4$, obtained by the oxidation of cumene procured from the pitch from pit-coal, and of cymene procured from camphor, and corresponding to an unknown glycol $C^9H^{12}O^2$*.

Insolinic acid $C^{10}H^{10}O^4$, corresponding to cumyl-glycol $C^{10}H^{14}O^2$*.

It is probable that these four latter acids are saturated; nevertheless, it has not yet been proved experimentally that they are incapable of uniting with chlorine or bromine by simple addition; their saturation is therefore as yet hypothetical.

NON-SATURATED ACIDS.—These belong to the series $C^nH^{2n-4}O^4$, and are:

Maleic and fumaric acids $C^4H^4O^4$, corresponding to a glycol $C^4H^8O^2$*.

Itaconic, citraconic, and mesaconic acids, $C^5H^6O^4$, corresponding to a glycol $C^5H^{10}O^2$*.

Camphoric acid $C^{10}H^{16}O^4$ also appears by its formula to belong to this series; but it is more probable that it belongs to a parallel series, the different terms of which are saturated. In fact, the camphorate of ethyl when acted upon by chlorine gives no product of addition, and Reboul has recently demonstrated that the non-saturated bodies retain their property of uniting directly with chlorine or bromine in the ethers they form.

There also exist other acids which contain four atoms of oxygen, such as orsellic acid $C^8H^8O^4$, parellic acid $C^9H^6O^4$, everninic acid $C^9H^{10}O^4$, etc., but these bodies are not sufficiently known for it to be certain whether they belong to this group or to another.

## STUDY OF THE MOST IMPORTANT ACIDS OF THIS GROUP.

**Oxalic Acid** ($C^2H^2O^4$).—Oxalic acid, the first term of the series of acids which correspond to the general formula $C^nH^{2n-2}O^4$, possesses a molecule which is much less stable than that of its homologues, and which therefore has peculiar properties.

PREPARATION.—Oxalic acid is formed when an organic substance is strongly oxidized. The most simple means of obtaining it consists in boiling sugar with very dilute nitric acid, and then crystallizing. This acid may also be extracted from several vegetables of the *Rumex* species, in which it exists in the state of acid salts. It is also extracted from the oxalate of potassium, which is produced in considerable quantity when impure cellulose (saw-dust) is submitted to the action of fused potash.

PROPERTIES.—1st. Oxalic acid is bibasic, and consequently forms, like its homologues, both acid and neutral salts, acid and neutral ethers, and two amides; it may also form quadr-acid salts resulting from the juxtaposition of a molecule of oxalic acid and a molecule of a bin-oxalate; such is the quadr-oxalate of potassium $\left(\left.\begin{matrix}C^2O^{2''}\\ KH\end{matrix}\right\}O^2 \quad \left.\begin{matrix}C^2O^{2''}\\ H^2\end{matrix}\right\}O^2\right)$. These latter bodies should be considered not as atomic combinations, but as molecular unions analogous to the compounds which contain water of crystallization.

2nd. Oxalic anhydride cannot exist. In every reaction leading to its production it splits up into oxide of carbon and carbonic anhydride. Thus all bodies having great affinity for water transform oxalic acid into a mixture of these two gases:

$$\underset{\text{Oxalic acid.}}{\left(\left.\begin{matrix}C^2O^{2''}\\ H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2''}\\ H^2\end{matrix}\right\}O^2\right)} = \underset{\text{Hydrate of sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2''}\\ H^2\end{matrix}\right\}O^2 + \text{aq.}\right)} + \underset{\text{Oxide of carbon.}}{(CO)} + \underset{\text{Carbonic anhydride.}}{(CO^2)}$$

3rd. Certain bodies, at the head of which glycerine may be placed, decompose oxalic acid into formic acid and carbonic anhydride by catalytic action:

$$\underset{\text{Oxalic acid.}}{(C^2H^2O^4)} = \underset{\text{Formic acid.}}{(CH^2O^2)} + \underset{\text{Carbonic anhydride.}}{(CO^2)}$$

4th. Chlorine and bromine seize the hydrogen of oxalic acid, and carbonic anhydride is formed:

$$\underset{\text{Oxalic acid.}}{\left(\left.\begin{matrix}C^2O^{2''}\\ H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Chlorine.}}{\left.\begin{matrix}Cl\\ Cl\end{matrix}\right\}} = \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\ Cl\end{matrix}\right\}\right)} + \underset{\text{Carbonic anhydride.}}{2(CO^2)}$$

Oxidizing agents act in the same way; only in this case water is formed instead of hydrochloric acid.

5th. Oxalic acid, heated with lime, produces carbonate of calcium and disengages hydrogen:

$$\underset{\text{Oxalic acid.}}{\left(\left.\begin{matrix}C^2O^{2''}\\ H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Lime.}}{2(CaO)} = \underset{\text{Carbonate of calcium.}}{2\left(\left.\begin{matrix}CO''\\ Ca''\end{matrix}\right\}O^2\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\ H\end{matrix}\right\}}$$

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6th. When the oxalates are calcined, oxide of carbon is disengaged, and a residue of carbonate is left:

$$\left(\begin{matrix}C^2O^{2\prime\prime}\\ Ca^{\prime\prime}\end{matrix}\right\} O^2\Big) = CO + \Big(\left.\begin{matrix}CO^{\prime\prime}\\ Ca^{\prime\prime}\end{matrix}\right\} O^2\Big)$$

Calcic oxalate. Oxide of carbon. Carbonate of calcium.

7th. The tendency of oxalic acid to lose its hydrogen, either in the state of water or of hydrochloric acid, makes it a reducing agent. It precipitates gold from its chloride, but does not act on chloride of platinum. Its reducing power is therefore less than that of formic acid, which reduces this chloride. These properties of oxalic and formic acids may be used to separate gold from platinum.

## TRIATOMIC ACIDS.

Triatomic alcohols may exchange $H^2$ for O, or $H^4$ for $O^2$, or $H^6$ for $O^3$. Thence three groups of acids, all triatomic like the alcohols from which they are derived.

Among these acids, the first, those which result from the substitution of O for $H^2$, are triatomic and monobasic; the second, those resulting from the substitution of $O^2$ for $H^4$, are triatomic and bibasic; the last, which contain three atoms of oxygen of substitution, are both triatomic and tribasic.

### TRIATOMIC AND MONOBASIC ACIDS.

These acids always contain four atoms of oxygen. It is possible that certain natural acids, the molecules of which contain $O^4$, belong to this group, but this is not yet demonstrated. As yet only four acids of this class are known with certainty. These are:

Glyceric acid $C^3H^6O^4$, corresponding to propyl-glycerine $C^3H^8O^3$.

Dioxybutyric acid $C^4H^8O^4$, corresponding to butyl-glycerine $C^4H^{10}O^3$*.

Oxysalicylic acid $C^7H^6O^4$, corresponding to oxysaligenin $C^4H^8O^3$*.

Eugenitic acid $C^{10}H^{12}O^4$, obtained by the reaction of sodium and carbonic anhydride on eugenic phenol (oil of cloves), and corresponding to an unknown glycerine $C^{11}H^{14}O^3$. These acids have not as yet been much studied; it is only known that, in their double decomposition with bases, they only exchange a single atom of hydrogen for positive metals.

It is probable that if these acids could be acted on by the perchloride of phosphorus, without being decomposed, they would give the trichlorides:

$$(C^3H^3OCl^3),\ (C^4H^5OCl^3),\ (C^7H^3OCl^3),\ \text{and}\ (C^{11}H^9OCl^3).$$

These chlorides, treated with water, would, according to all appearance, furnish:

| | |
|---|---|
| The first, bichloro-propionic acid | $C^3H^4Cl^2O^2$. |
| The second, bichloro-butyric acid | $C^4H^6Cl^2O^2$. |
| The third, bichloro-benzoic acid | $C^7H^4Cl^2O^2$. |
| The last, an acid | $C^{11}H^{10}Cl^2O^2$. |

$$\underset{\text{Chloride of glyceryl (unknown).}}{(C^3H^3OCl^3)} + \underset{\text{Water.}}{(H^2O)} = \underset{\text{Hydrochloric acid.}}{(HCl)} + \underset{\text{Bichloro-propionic acid.}}{(C^3H^4Cl^2O^2)}.$$

In reality, of the three atoms of typical hydrogen which form the three groups OH for which chlorine may be substituted, only one is basic, the others are alcoholic. Now, the organic chlorides in which chlorine is substituted for the residues OH of which the hydrogen is alcoholic, cannot be decomposed by water, while those in which the chlorine is substituted for the residues OH containing basic hydrogen, are capable, under the influence of water, of regaining the residue OH in exchange for their chlorine.

It is also probable that on operating on these trichlorides in the same way as on chloride of lactyl, mono, bi, tri, alcoholic ethers would be obtained; and that moreover there might be procured two isomeric bi-alcoholic ethers and two isomeric mono-alcoholic ethers, the first neutral, the others acid.

In a word, glyceric acid ought to be able to give rise to derivatives analogous to those furnished by lactic acid, but more numerous, because it possesses three atoms of typical hydrogen while lactic acid only contains two.*

## TRIATOMIC AND BIBASIC ACIDS.

No acid of this order has as yet been obtained by the direct oxidation of the corresponding alcohols. But, two acids are known, of which one certainly, and the other probably, belongs to this group. These are:

Tartronic acid ($C^5H^4O^5$), obtained by the spontaneous decomposition of nitrotartaric acid; and malic acid ($C^4H^6O^5$), obtained by the action of moist oxide of silver on monobromo-succinic acid, and which also exists in many vegetable products.

As malic acid is the only acid of this group which has been much studied, we will confine our remarks to it.

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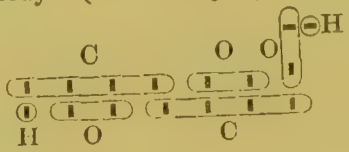
* In the first edition glyoxylic acid, $C^2H^4O^4$, was included among the monobasic triatomic acids. Since then, Dr. Debus has demonstrated that the formula of this acid is $C^2H^2O^3$, and that a triatomic acid of the formula $C^2H^4O^4$ is impossible, because it would require that 2OH should be fixed on the same atom of carbon, of which we would have no established example. According to this new formula, glyoxylic acid would be a half-acid, half-aldehyd body. (*See* Aldehyds.)



**Malic Acid** $\left(C^4H^3O^{2'''}\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.\right)$.—PREPARATION.—1st. Malic acid may be prepared synthetically by means of moist oxide of silver and monobromo-succinic acid :

$$\underset{\text{Bromosuccinic acid.}}{2\left(C^4H^3O^{2'''}\left\{\begin{matrix}Br\\OH\\OH\end{matrix}\right.\right)} + \underset{\text{Oxide of silver.}}{\left(\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Malic acid.}}{2\left(C^4H^3O^{2'''}\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.\right)}$$

$$+ \underset{\text{Bromide of silver.}}{2\left(\left.\begin{matrix}Ag\\Br\end{matrix}\right\}\right)}$$

This method of preparation, though very interesting from a theoretical point of view, has no practical utility.

2nd. Malic acid may also be obtained by causing nitrous acid to act on asparagin (malo-diamide), or on aspartic acid (malic monamide) :

$$\underset{\text{Asparagin.}}{\left[\left.\begin{matrix}\left(C^4H^3O^{2'''}\left\{\begin{matrix}OH\\ :\end{matrix}\right.\right)''\\H^2\\H^2\end{matrix}\right\}N^2\right]} + \underset{\text{Nitrous acid.}}{2\left(\left.\begin{matrix}NO\\H\end{matrix}\right\}O\right)} = \underset{\text{Nitrogen.}}{2\left(\left.\begin{matrix}N\\N\end{matrix}\right\}\right)}$$

$$+ \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Malic acid.}}{\left(C^4H^3O^{2'''}\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.\right)}$$

3rd. Malic acid occurs ready formed in a number of vegetables whence it may be extracted. It is usually taken from the berries of the service-tree, which yield it very plentifully.

These berries, either ripe or not, are crushed, and the juice extracted, clarified by boiling with white of egg, and digested with a slight excess of carbonate of lead, which is added gradually till effervescence ceases. Different insoluble plumbic salts are thus formed, and among them malate of lead, which is scarcely soluble in the cold, but is rendered more soluble by heat.

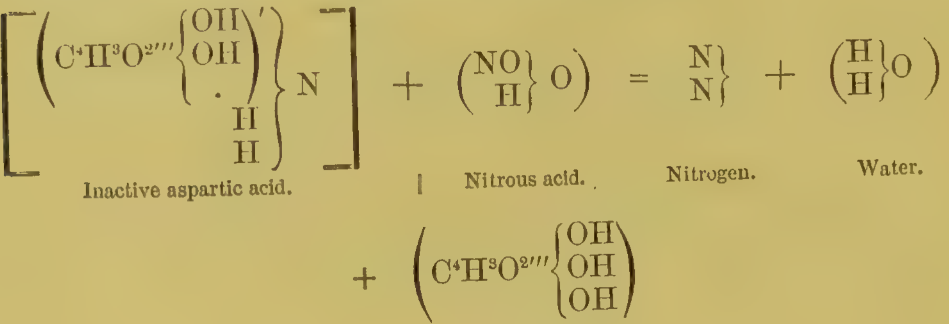
When the liquid becomes cold it is filtered, and the precipitate after being washed several times with cold water, is boiled with water and filtered while hot. On cooling, brilliant needles of malate of lead are deposited and separated by filtration. The liquid which contained these needles is again boiled with the residue of the first treatment, and the operation is thus continued until plumbic malate is no longer deposited.

The malate of lead thus obtained is pulverized, suspended in water, and decomposed by a current of hydrosulphuric acid. Then it is filtered to remove the sulphide of lead precipitated, and the filtered liquid is boiled to free it from the excess of sulphuretted hydrogen, and evaporated to the consistence of a thick syrup, which, on standing some time, deposits crystallized malic acid.

This malic acid, however, is not pure; it contains tartaric and citric acids, and tartrate of calcium. In order to purify it, instead of evaporating its solution to a syrupy consistence, it must be divided into two equal parts, one of these exactly saturated with ammonia, and then the two again mixed. Bimalate of ammonium is thus formed. This salt crystallizes very readily, and may easily be separated from the other bodies with which it is mixed by two or three crystallizations from water.

When the ammonic bimalate is pure, it is dissolved in water, and its solution precipitated by acetate of lead. The precipitate is well washed and suspended in water, through which a current of sulphuretted hydrogen is transmitted until the decomposition is complete, after which the liquid is filtered, evaporated to a syrupy consistence, and left to crystallize.

The malic acid extracted from the berries of the service-tree, or obtained from asparagin or natural aspartic acid, is levogyrate. That formed by the action of oxide of silver on bromo-succinic acid is, on the contrary, quite inactive. An inactive malic acid is also obtained by treating nitrous acid with inactive aspartic acid:

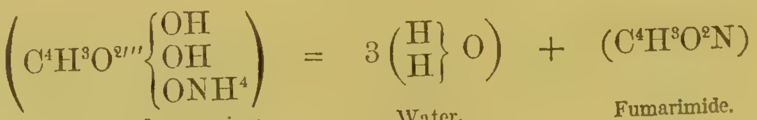


$$\left[\left.\begin{matrix}\left(\mathrm{C^4H^3O^{2'''}}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \cdot\end{matrix}\right.\right)'\\ \mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{N}\right] + \left(\left.\begin{matrix}\mathrm{NO}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right) = \left.\begin{matrix}\mathrm{N}\\ \mathrm{N}\end{matrix}\right\} + \left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right) + \left(\mathrm{C^4H^3O^{2'''}}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\right.\right)$$

Inactive aspartic acid. Nitrous acid. Nitrogen. Water.

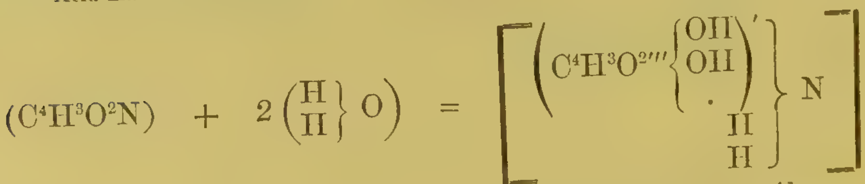
Inactive malic acid.

This inactive aspartic acid is prepared by boiling with hydrychloric acid the fumarimide produced when acid malate of ammonium is exposed for several hours to a temperature of 160°—200°:



$$\left(\mathrm{C^4H^3O^{2'''}}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{ONH^4}\end{matrix}\right.\right) = 3\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right) + (\mathrm{C^4H^3O^2N})$$

Acid malate of ammonium. Water. Fumarimide.



$$(\mathrm{C^4H^3O^2N}) + 2\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right) = \left[\left.\begin{matrix}\left(\mathrm{C^4H^3O^{2'''}}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \cdot\end{matrix}\right.\right)'\\ \mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{N}\right]$$

Fumarimide. Water. Aspartic (malamic) acid.

PROPERTIES.—The aqueous solution of active malic acid, when evaporated to a syrupy consistence, and left in a warm place, deposits this acid in the form of small lumps composed of four- or six-sided prisms. It melts at 100° (Pasteur), but does not lose weight at 120°; it has a very acid taste, and is very soluble in water, and deliquescent.

Its aqueous solution is levogyrate. When saturated by bases it is sometimes levogyrate and sometimes dextrogyrate. Organic or mineral acids have a tendency to make it become levogyrate.

Inactive malic acid crystallizes more readily than that possessing rotatory power; it is less soluble in water, is not deliquescent, and does not melt below 133°.

When heated to 176°, malic acid loses a molecule of water, and is transformed into two new acids; maleic and fumaric acids ($C^4H^4O^4$). (*see* Non-saturated Biatomic and Bibasic Acids). These bodies are not anhydrides of malic acid. They are biatomic, while the first anhydride of malic acid could not have an atomicity greater than unity. They therefore result from a more complete decomposition, and one of the atoms of hydrogen which goes to form the water eliminated must have been furnished by the radicle of the malic acid.

Malic acid loses an atom of oxygen when heated with hydriodic acid, and returns to the state of succinic acid; iodine is set free. The cause of this phenomenon is the same as that of the reduction of lactic into propionic acid. Probably a malic iodhydrin is first formed, which, on contact with an excess of hydriodic acid, gives iodine and succinic acid.

The solution of malic acid is very acid; it can never be completely saturated by earthy carbonates, unless it be by carbonate of magnesium: when impure it becomes mouldy by keeping.

The solution of malic acid does not precipitate either lime or baryta water, nor the solutions of nitrate of silver or nitrate of lead, but it precipitates mercurous nitrate. With acetate of lead it gives a precipitate which becomes crystalline when left for some time in the liquor whence it arises. It reduces the salts of gold.

Heated to a temperature of 150° with an excess of potash, malic acid is transformed into acetate and oxalate, disengaging hydrogen:

$$\underset{\text{Malic acid.}}{(C^4H^6O^5)} + \underset{\text{Hydrate of potassium.}}{3\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Oxalate of potassium.}}{(C^2K^2O^4)}$$

$$+ \underset{\text{Acetate of potassium.}}{(C^2H^3KO^2)} + \underset{\text{Water.}}{2\,(H^2O)} + \underset{\text{Hydrogen.}}{H^2}$$

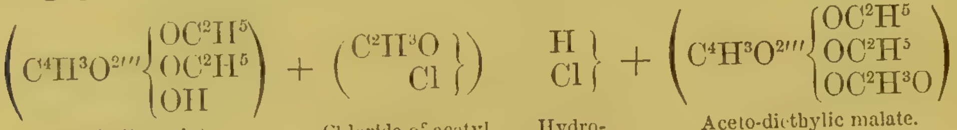
Ferments transform it into succinic and even into butyric acid.

Malic acid contains two atoms of hydrogen which may be replaced by metals, and can form a series of acid salts answering to the general formula $\left(C^4H^3O^{2'''}\left\{\begin{matrix}OM'\\OH\\OH\end{matrix}\right.\right)$, and a series of neutral salts whose general formula is $\left(C^4H^3O^{''''}\left\{\begin{matrix}OM'\\OM'\\OH\end{matrix}\right.\right)$; it is therefore a bibasic acid. But besides these two atoms of basic hydrogen, malic acid also contains a third atom of hydrogen, united to the carbon by means of oxygen, and is triatomic. There are numerous proofs of its triatomicity.

Every time a new atom of oxygen of addition is introduced into an acid or an alcohol, the atomicity of these bodies increases by unity. Malic acid, derived from biatomic succinic acid by the addition of an atom of oxygen, ought therefore to contain an atom of typical hydrogen more than the latter; it should be triatomic.

Neutral bialcoholic malic ethers, and acid monoalcoholic ethers acting as monobasic, are known; it is probable that acid monoalcoholic bibasic ethers, acid bialcoholic ethers, and trialcoholic ethers might also be prepared. Perhaps trialcoholic ether might be obtained by substituting potassium for hydrogen in the neutral bialcoholic ether, and by treating this potassic product by an hydriodic ether.

Recently the atom of typical hydrogen still contained in the bialcoholic ethers of malic acid has been replaced by acetyl. This is done by heating these ethers with chloride of acetyl. Hydrochloric acid is disengaged during the reaction:



$$\left(C^4H^3O^{2'''}\left\{\begin{matrix}OC^2H^5\\OC^2H^5\\OH\end{matrix}\right.\right) + \left(\begin{matrix}C^2H^3O\\Cl\end{matrix}\right\}\right) \quad \left.\begin{matrix}H\\Cl\end{matrix}\right\} + \left(C^4H^3O^{2'''}\left\{\begin{matrix}OC^2H^5\\OC^2H^5\\OC^2H^3O\end{matrix}\right.\right)$$

Diethylic malate. Chloride of acetyl. Hydrochloric acid. Aceto-diethylic malate.

Malic acid ought also to form several amides: 1st, a neutral triamide; 2nd, a neutral and an acid diamide; 3rd, an acid monobasic monamide and an acid bibasic monamide. Three of these bodies are known, viz., the neutral diamide obtained by causing ammonia to act on diethylic malate, acid diamide or asparagin, which is found in the vegetable kingdom, and an acid bibasic monamide, aspartic acid, which is derived from asparagin by the action of bases.

The production of these different bodies is very difficult, as the molecule of malic acid is already much too complicated to resist the action of pentachloride of phosphorus, and the formation of the chlorides is the most convenient method of preparing the different derivatives of the acids.

## TRIATOMIC AND TRIBASIC ACIDS.

Only a very few acids of this class are known with certainty; the most important are: aconitic acid $C^6H^6O^6$, and carballylic acid $C^6H^8O^6$. The latter has been obtained by the action of nascent hydrogen on aconitic acid. Maxwell Simpson has also prepared it by causing alcoholic solution of potash to act on the tricyanide of glyceryl ($C^3H^5(CN)^3$):

$$\underset{\text{Cyanide of glyceryl.}}{\left(C^3H^{5'''}\left\{\begin{matrix}CN\\CN\\CN\end{matrix}\right.\right)} + \underset{\text{Potash.}}{3\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Ammonia.}}{3(NH^3)}$$

$$+ \underset{\text{Potassic salt of the new acid.}}{\left(C^3H^{5'''}\left\{\begin{matrix}CO^2K\\CO^2K\\CO^2K\end{matrix}\right.\right)}$$

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This acid corresponds to a hexylic glycerine $C^6H^{14}O^3$*, from which it differs by the substitution of $O^3$ for $H^6$.

Carballylic acid has not been much studied, but it cannot be doubted that it possesses the properties:

1st. Of forming two series of acid salts and one series of neutral salts.

2nd. Of forming three series of ethers; the first monoalcoholic and bibasic, the second bialcoholic and monobasic, the last trialcoholic and neutral.

3rd. Of giving rise to acid bibasic monamides, to acid monobasic diamides, and to neutral triamides.

It is possible that if, in Maxwell Simpson's acid, an atom of bromine were substituted for an atom of hydrogen, and then moist oxide of silver were made to act on this body, citric acid would be obtained synthetically:

$$\underset{\text{Bromo-carballylic acid.}}{2(C^6H^7BrO^6)} + \underset{\text{Oxide of silver.}}{(Ag^2O)} + \underset{\text{Water.}}{(H^2O)} = \underset{\text{Citric acid.}}{2(C^6H^8O^7)} + \underset{\text{Bromide of silver.}}{2(AgBr)}$$

Aconitic acid may be extracted from the *Aconitum napellus*, in which it exists ready formed, but it is more easily prepared by decomposing citric acid by heat. For this purpose citric acid is heated in a retort until oily streaks appear in the receiver. The operation is then arrested, the residue contained in the retort is dissolved in five times its weight of absolute alcohol, and the solution is submitted to the action of a current of dry hydrochloric acid gas. When this acid ceases to be absorbed, the solution is precipitated by water, and an oily layer of aconitic ether forms. This ether is saponified by an alkali, the alkaline solution is precipitated by acetate of lead, and the aconitate of lead suspended in water is submitted to the action of a current of hydrosulphuric acid. Sulphide of lead and aconitic acid are formed; they are separated by filtration, and the solution of aconitic acid is evaporated.

This acid is very soluble in water, alcohol, and ether. When heated, it becomes brown at 130°, is liquefied at 140°, and boils at 160°; it then decomposes into carbonic anhydride and itaconic acid:

$$\underset{\text{Aconitic acid.}}{(C^6H^6O^6)} = \underset{\text{Carbonic anhydride.}}{(CO^2)} + \underset{\text{Itaconic acid.}}{(C^5H^6O^4)}$$

Aconitic acid is converted into succinic acid when the aconitate of calcium is fermented in contact with cheese.

It is a triatomic and tribasic acid, and gives two series of acid and one of neutral salts.

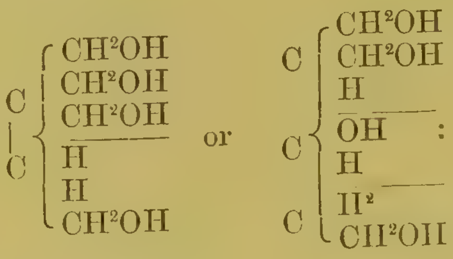
## TETRATOMIC ACIDS.

We ought to be able to obtain these acids by the direct oxidation of tetratomic alcohols. In fact, erythrite in concentrated solution gives an acid when acted on by platinum black, but this acid, which is probably tetratomic, has not as yet been studied.

In the ordinary tetratomic alcohols which contain 2OH grouped as $(CH^2OH)$ or $(CHOH)$, the substitution of O for $H^2$ is only possible twice. But in tetratomic alcohols containing three or four times the group $(CH^2OH)$, this substitution would be possible three or four times. The former alcohols can only therefore give rise to mono- or bibasic tetratomic acids; the latter would form tetratomic mono, bi, tri, and tetrabasic acids.

In fact, five tetratomic acids are known: two of them are monobasic, these are gallic acid $(C^7H^6O^5)$* and erythric acid $(C^4H^8O^5)$?; two are bibasic, tartaric acid $(C^4H^6O^6)$ and an acid $(C^5H^8O^6)$ still unnamed, obtained by Kékulé by treating dibromopyrotartaric acid by moist oxide of silver. The fifth, citric acid $(C^6H^8O^7)$, is tribasic.

Erythric acid is derived from erythrite $(C^4H^{10}O^4)$ by the substitution of O for $H^2$. Tartaric acid also appears to be derived from this same alcohol by the substitution of $O^2$ for $H^4$. The alcohol corresponding to citric acid is still unknown: its rough formula would be $(C^6H^{14}O^4)$, and its rational formula:



$$\begin{array}{c} C \\ | \\ C \end{array}\left\{\begin{array}{l} CH^2OH \\ CH^2OH \\ CH^2OH \\ \hline H \\ H \\ CH^2OH \end{array}\right. \quad \text{or} \quad \begin{array}{c} C \\ \\ C \\ \\ C \end{array}\left\{\begin{array}{l} CH^2OH \\ CH^2OH \\ H \\ \hline OH \\ H \\ \hline H^2 \\ CH^2OH \end{array}\right. :$$

it would belong to the hexylic series.

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* Grimaux was the first to consider gallic acid as tetratomic and monobasic.

**Gallic Acid** $\left(\left.\begin{matrix}C^7H^2O^{iv}\\H^4\end{matrix}\right\}O^4 + aq.\right)$.—This acid exists ready formed in a large number of vegetables, and is readily prepared by the transformation of a substance contained in the gall-nut, known as tannin or gallotannic acid.

The most simple method is to leave powdered gall-nuts moistened with water for some weeks at a temperature of 20° or 25°: the mass swells and becomes mouldy. In about a month it is pressed, and the water, which contains much colouring matter but very little gallic acid, is thrown away; the residue is then digested in boiling water, from which crystals of impure gallic acid are deposited on cooling. These crystals are purified by being again dissolved in seven or eight times their weight of boiling water, and bleaching the solution by animal charcoal.

Tannin may also be transformed into gallic acid by heating it with dilute mineral acids or with alkaline solutions. The latter method is the least to be recommended, inasmuch as the alkalies decompose the gallic acid as it is formed. The dilute acids give better results and allow the operation to be conducted rapidly. According to Stenhouse, the best method consists in digesting tannin for a day with sulphuric acid diluted with seven or eight times its weight of water, care being taken to occasionally replace the water evaporated. The liquid, concentrated at a gentle heat, deposits crystals of gallic acid which are scarcely coloured, and the weight of which is almost equal to that of the tannin employed.

Gallic acid crystallizes in long silky needles. The crystals have a slightly-acid taste, but are without odour; they dissolve in 100 parts of cold and 3 parts of boiling water; alcohol and ether also dissolve them: they contain a molecule of water of crystallization, which they lose when dried at 100°.

Heated to 210° or 215°, gallic acid is decomposed into pyrogallic phenol and carbonic anhydride:

$$\begin{array}{ccccc} (C^7H^6O^5) & = & (CO^2) & + & (C^6H^6O^3) \\ \text{Gallic acid.} & & \text{Carbonic anhydride.} & & \text{Pyrogallic phenol.} \end{array}$$

When protected from the air the solution of gallic acid is preserved unaltered, but when exposed to the air it absorbs oxygen and deposits a black sediment. This oxidation becomes very rapid under the influence of the alkalies: the liquid then assumes a red colour.

Gallic acid colours ferric salts deep blue. It does not precipitate vegetable alkalies nor gelatine when pure, but when mixed with gum it precipitates gelatine.

When gently heated with concentrated sulphuric acid, gallic acid loses a molecule of water and is converted into rufigallic acid:

$$\begin{array}{ccccc} (C^7H^6O^5) & = & (H^2O) & + & (C^7H^4O^4) \\ \text{Gallic acid.} & & \text{Water.} & & \text{Rufigallic acid.} \end{array}$$

Gallic acid has been recently obtained by Lautemann by the reaction of moist oxide of silver on dibromosalicylic acid:

$$\underset{\text{Dibromo-salicylic acid.}}{(C^7H^4Br^2O^3)} + \underset{\text{Oxide of silver.}}{(Ag^2O)} + \underset{\text{Water.}}{(H^2O)} = \underset{\text{Bromide of silver.}}{2\left(\left.\begin{matrix}Ag\\Br\end{matrix}\right\}\right)} + \underset{\text{Gallic acid.}}{(C^7H^6O^5)}$$

## *Appendix to Gallic Acid.*

**Tannin.**—Gall-nuts, coffee, oak bark, and many other vegetables or parts of vegetables contain substances which precipitate albumen, gelatine, and the vegetable alkaloids, and which form insoluble compounds with the skin of animals, fibrine, etc. The generic name of tannins is given to all these substances, but they nevertheless differ from each other.

Only one of these tannins is accurately known—that procured from the gall-nut—and we will confine our remarks to it.

In order to extract tannin or gallotannic acid from gall-nuts, these are powdered, and digested with dilute ether in a percolator. As the liquid percolates through the gall-nuts, these yield their tannic acid to the water, while the ether dissolves the fatty matters and colouring substances. On standing, these solutions separate into two layers, the lower of which containing the tannin is removed, and evaporated at 100°: the tannin is procured in the form of a vitreous, yellowish, very light substance, which on being reduced to powder presents the appearance of crystalline plates, though in reality it is not crystallized.

Tannin is soluble in water, alcohol, and ether; it precipitates the ferric salts a very dark blue, almost black, but has no action on the ferrous salts, which fact explains why ordinary ink, obtained by boiling a solution of a ferrous salt with gall-nuts, becomes darker when exposed to the air.

Tannin possesses acid properties, and enters into double decomposition with bases, but its alkaline salts are difficult to obtain, because, on contact with the alkalies and air, tannin oxidizes, and is transformed into a dark-red substance, identical with that which is formed when gallic acid is submitted to the same reaction.

Tannin transforms skins into leather: so great is their affinity that when a piece of skin is placed in an aqueous solution of tannin, this skin seizes the whole of the tannin in solution. The process of tanning is founded on this property.

Dissolved in water and left in the air in presence of ferments, tannin is changed into gallic acid; the same transformation takes place under the influence of boiling dilute acids or of alkaline solutions. Chemists are not agreed as to the reaction which takes place in this case. According to some, the tannin simply oxidizes and produces gallic acid, water and carbonic anhydride being formed at the same time:

$$\underset{\text{Tannin.}}{(C^{27}H^{22}O^{17})} + \underset{\text{Oxygen.}}{6\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\right)} = \underset{\text{Carbonic anhydride.}}{6(CO^2)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

$$+ \underset{\text{Gallic acid.}}{3(C^7H^6O^5)}$$

According to Strecker, on the contrary, tannin is a glucoside, which is transformed into gallic acid and glucose on absorbing the elements of water. The carbonic anhydride, according to his view, is owing to the fermentation of glucose; the following would be the equation according to this hypothesis:

$$\underset{\text{Tannin.}}{(C^{27}H^{22}O^{17})} + \underset{\text{Water.}}{5(H^2O)} = \underset{\text{Gallic acid.}}{3(C^7H^6O^5)} + \underset{\text{Glucose.}}{(C^6H^{12}O^6 + aq.)}$$

However, the late experiments of Messrs. Kawalier and Knop tend to prove that tannin is not a glucoside, and that the glucose which is sometimes formed during its transformation into gallic acid is owing to impurities. Tannin not being crystallizable, its purification is very difficult.

**Tartaric Acid.**—There exist several varieties of tartaric acid which differ in their crystalline form and by their rotatory power; these are: dextrotartaric or dextroracemic acid, lævotartaric or lævoracemic acid, inactive tartaric acid, paratartaric or racemic acid, and artificial paratartaric acid.

Dextrotartaric or the ordinary acid, thus called because it is dextrogyrate, is extracted from the cream of tartar of wine casks, which is an acid tartrate of potassium ($C^4H^5KO^6$). After purifying this salt by several crystallizations from boiling water, it is again dissolved, and milk of lime or powdered chalk is added to the solution. In both cases neutral tartrate of calcium is precipitated, and neutral potassic tartrate remains dissolved:

$$\underset{\text{Acid tartrate of potassium.}}{2(C^4H^5KO^6)} + \underset{\text{Lime.}}{(CaO)} = \underset{\text{Neutral tartrate of potassium.}}{(C^4H^4K^2O^6)} + \underset{\text{Neutral tartrate of calcium.}}{(C^4H^4Ca''O^6)} + \underset{\text{Water.}}{(H^2O)}$$

When chalk is used, the reaction is accompanied by a violent disengagement of carbonic anhydride. The operation is arrested when effervescence ceases and the liquid is neutral.

It is then filtered, and chloride of calcium is added to the filtered liquid; all the tartrate of potassium is transformed into tartrate of calcium which precipitates, and potassic chloride which remains in solution:

$$\underset{\text{Neutral tartrate of potassium.}}{(C^4H^4K^2O^6)} + \underset{\text{Chloride of calcium.}}{(Ca''Cl^2)} = \underset{\text{Chloride of potassium.}}{2(KCl)} + \underset{\text{Tartrate of calcium.}}{(C^4H^4Ca''O^6)}$$

The precipitate of tartrate of calcium is suspended in water, and sulphuric acid is added, when insoluble sulphate of calcium and soluble tartaric acid are formed:

$$\underset{\text{Calcic tartrate.}}{(C^4H^4Ca''O^6)} + \underset{\text{Sulphuric acid.}}{(SH^2O^4)} = \underset{\text{Sulphate of calcium.}}{(SCaO^4)} + \underset{\text{Tartaric acid.}}{(C^4H^6O^6)}$$

The liquid is filtered, evaporated, and left to cool; tartaric acid crystallizes in large crystals, which are hemihedral to the right.

Acid paratartrate of potassium is found in the cream of tartar of Austria, Hungary, Saintonge, etc. After extracting the acid from this cream of tartar in the manner just described, paratartaric may be separated from tartaric acid by repeated crystallizations. Paratartaric acid crystallizes in small needles, which stand out white upon the large crystals of tartaric acid, and may be readily separated mechanically. Paratartaric acid may also be obtained artificially, by submitting tartaric ether or the tartrate of cinchonine to the action of heat: this acid is without action on polarized light; its crystals and those of its salts do not present hemihedral facets.

When the double paratartrate of sodium and ammonium is crystallized there is a mixture of crystals, some of which are hemihedral to the right and some to the left. If these crystals be separated mechanically and the corresponding acid be prepared from each, it will be found that this acid is no longer paratartaric, but tartaric acid. But the acid prepared from those crystals which are hemihedral to the right is ordinary tartaric acid, while that prepared from those hemihedral to the left presents, like the salt whence it arises, hemihedral facets turned to the left, and deviates the plane of polarized light to the left; this is lævotartaric or lævoracemic acid.

As lævoracemic acid is not destroyed by fermentation, while dextroracemic acid is, this property may be utilized in its preparation. If paratartaric acid be fermented and the acid contained in the liquid be extracted when the fermentation is terminated, lævoracemic acid can be obtained.

Lævoracemic and dextroracemic acids combine, producing heat, and forming paratartaric acid.

Paratartaric acid therefore has a double molecule, and owes its inactivity to the fact that the dextrogyrate action of one of the groups it contains is neutralized by the contrary action of the other group.

Under the influence of a temperature of 170°, maintained for several hours, paratartrate of cinchonine is modified and inactive tartaric acid may then be extracted from it: this acid differs from paratartaric acid in that its inactivity is absolute, and is not owing to a compensating influence

An acid which possesses the composition and most of the properties of paratartaric acid has recently been produced artificially by submitting dibromo-succinic acid to the action of moist oxide of silver:

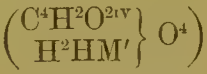
$$\underset{\text{Dibromo-succinic acid.}}{(C^4H^4Br^2O^4)} + \underset{\text{Oxide of silver.}}{(Ag^2O)} + \underset{\text{Water.}}{(H^2O)} = \underset{\text{Bromide of silver.}}{2(AgBr)} + \underset{\text{Artificial paratartaric acid.}}{(C^4H^6O^6)}$$

This acid differs from true paratartaric acid in that it does not possess the property of dividing into two acids having different optical properties.

Chemical Properties of Tartaric Acid.—The different modifications of tartaric acid should be regarded as so many allotropic states of one compound. In reality, the chemical properties of a slightly elevated order are the same for all these bodies.

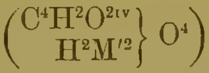
1st. Tartaric acid is tetratomic. When the basic tartrate of lead ($PbO,C^4H^4PbO^6$) is dried at 130°, a molecule of water is eliminated, and a tartrate ($C^4H^2Pb^2O^6$) is produced, in which four atoms of hydrogen are replaced by two atoms of lead; this metal here acting with a value of substitution equal to two.

2nd. Tartaric acid is bibasic; therefore, with positive metals, it forms two series of salts; the first, acid or monometallic; the others, neutral or bimetallic. These salts should be represented by the formulæ:



$$\left(\left.\begin{matrix}C^4H^2O^{2iv}\\H^2HM'\end{matrix}\right\}O^4\right)$$

Acid tartrate.

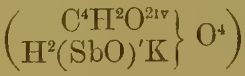


$$\left(\left.\begin{matrix}C^4H^2O^{2iv}\\H^2M'^2\end{matrix}\right\}O^4\right)$$

Neutral tartrate.

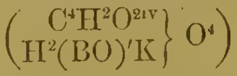
3rd. When a monometallic tartrate reacts on a polyatomic base, such as hydrate of antimony $\left(\left.\begin{matrix}Sb''\\H^3\end{matrix}\right\}O^3\right)$, ferric hydrate $\left(\left.\begin{matrix}Fe^{2vi}\\H^6\end{matrix}\right\}O^6\right)$, or even on certain acids or weak acid anhydrides, such as boracic acid $\left(\left.\begin{matrix}B'''\\H^3\end{matrix}\right\}O^3\right)$, or arsenious anhydride ($As^2O^3$), the second atom of basic hydrogen is replaced by an oxygenized group, and particular salts are obtained, which are:—

Tartar emetic, or potassic tartrate of antimony:



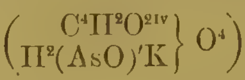
$$\left(\left.\begin{matrix}C^4H^2O^{2iv}\\H^2(SbO)'K\end{matrix}\right\}O^4\right)$$

Soluble cream of tartar, or potassic tartrate of boron:



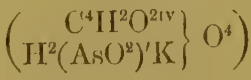
$$\left(\left.\begin{matrix}C^4H^2O^{2iv}\\H^2(BO)'K\end{matrix}\right\}O^4\right)$$

Arsenious potassic tartrate, or potassic tartrate of arsenic:



$$\left(\left.\begin{matrix}C^4H^2O^{2iv}\\H^2(AsO)'K\end{matrix}\right\}O^4\right)$$

Arsenic potassic tartrate:



$$\left(\left.\begin{matrix}C^4H^2O^{2iv}\\H^2(AsO^2)'K\end{matrix}\right\}O^4\right)$$

Potassic tartrate of bismuth:

$$\left(\left.\begin{matrix}C^4H^2O^{2\,iv}\\ H^2(BiO)'K\end{matrix}\right\}O^4\right)$$

Potassic tartrate of uranium:

$$\left(\left.\begin{matrix}C^4H^2O^{2\,iv}\\ H^2(UO)'K\end{matrix}\right\}O^4\right)$$

Potassic tartrate of chromium:

$$\left(\left.\begin{matrix}C^4H^2O^{2\,iv}\\ H^2(CrO)'K\end{matrix}\right\}O^4\right)$$

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Potassic tartrate of iron:

$$\left(\left.\begin{matrix}(C^4H^2O^{2\,iv})^2\\ H^4(Fe^2O^2)''K^2\end{matrix}\right\}O^8\right)$$

In these different compounds the potassium may be replaced by another monatomic metal, or even by another biatomic metal. But in the case of those bodies which only contain a single atom of potassium, this latter substitution entails the doubling of the molecule.

The potassic tartrate of antimony (tartar emetic) is obtained by boiling for half an hour a mixture of three parts of oxide of antimony and four parts of cream of tartar diluted with water. The boiling liquid is filtered, and the tartar emetic is deposited in crystals on cooling; these crystals have the formula:

$$\left(\left.\begin{matrix}C^4H^2O^{2\,iv}\\ H^2(SbO)'K\end{matrix}\right\}O^4\right)^2 + Aq.$$

When heated to 100°, tartar emetic loses its water of crystallization. It dissolves in water readily. Ammonia scarcely affects this solution when it is diluted, but if it be concentrated and hot, this reagent produces a white flaky precipitate of antimonious hydrate. In such a solution potash forms a white precipitate soluble in an excess of the reagent, and the mineral acids, such as nitric, sulphuric, or hydrochloric acid, give a white precipitate of a sub-salt of antimony:

$$\underset{\text{Tartar emetic.}}{\left(\left.\begin{matrix}C^4H^2O^{2\,iv}\\ H^2(SbO)'K\end{matrix}\right\}O^4\right)} + \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\ Cl\end{matrix}\right\}\right)} = \underset{\text{Chloride of potassium.}}{\left.\begin{matrix}K\\ Cl\end{matrix}\right\}} + \underset{\text{Tartaric acid.}}{\left(\left.\begin{matrix}C^4H^2O^{2\,iv}\\ H^4\end{matrix}\right\}O^4\right)}$$

$$+ \underset{\text{Oxychloride of antimony.}}{(SbO'Cl)}$$

In solutions of tartar emetic, tannic acid produces a white precipitate of tannate of antimony. It is the only organic acid which possesses this property.

Tartar emetic added to solutions of the nitrates of silver, calcium, barium, or strontium, gives potassic nitrate and a double tartrate of antimony and silver or calcium, etc., which is precipitated.

Heated to 200°, all these double tartrates lose water, which is formed at the expense, not of the basic but of the typical hydrogen of the tartaric acid, and of the oxygen of the radicle (SbO)′ :

$$\underset{\text{Tartar emetic.}}{\left(\left.\begin{matrix}\mathrm{C^4H^2O^{2iv}}\\ \mathrm{H^2(SbO)'K}\end{matrix}\right\}\mathrm{O^4}\right)} = \underset{\text{Water.}}{\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}} + \underset{\text{Dried tartar emetic.}}{\left(\left.\begin{matrix}\mathrm{C^4H^2O^{2iv}}\\ \mathrm{Sb'''K}\end{matrix}\right\}\mathrm{O^4}\right)}$$

These dried potassic tartrates are tetrametallic tartrates, in which a single atom of hydrogen is replaced by potassium, and the three others by a trivalent element.

4th. If tartaric acid be kept in a state of fusion for some time, it loses half a molecule of water, and ditartaric acid $\left(\left.\begin{matrix}\mathrm{(C^4H^2O^{2iv})^2}\\ \mathrm{H^6}\end{matrix}\right\}\mathrm{O^7}\right)$ is produced. If the action of heat be maintained still longer, the tartaric acid loses a whole molecule of water, and furnishes anhydrous tartaric acid ($\mathrm{C^4H^4O^5}$).

Anhydrous tartaric acid can exchange an atom of hydrogen for an atom of metal: such compounds are obtained by adding a solution of this body to that of the acetate of calcium, barium, or strontium.

If it be heated to 150° with an excess of massicot, it loses another molecule of water and gives a salt which results from the substitution of Pb for $\mathrm{H^2}$.

The first tartaric anhydride is therefore a biatomic acid, which is another proof in favour of the tetratomicity of tartaric acid.

5th. When tartaric acid is strongly heated, the tartaric group is destroyed, water and carbonic anhydride are disengaged, and pyruvic acid ($\mathrm{C^3H^4O^3}$) or pyrotartaric acid ($\mathrm{C^5H^8O^4}$) is formed :

$$\underset{\text{Tartaric acid.}}{\mathrm{(C^4H^6O^6)}} = \underset{\substack{\text{Carbonic}\\ \text{anhydride.}}}{\mathrm{(CO^2)}} + \underset{\text{Water.}}{\mathrm{(H^2O)}} + \underset{\text{Pyruvic acid.}}{\mathrm{(C^3H^4O^3)}}$$

$$\underset{\text{Tartaric acid.}}{\mathrm{2(C^4H^6O^6)}} = \underset{\substack{\text{Carbonic}\\ \text{anhydride.}}}{\mathrm{3(CO^2)}} + \underset{\text{Water.}}{\mathrm{2(H^2O)}} + \underset{\substack{\text{Pyrotartaric}\\ \text{acid.}}}{\mathrm{(C^5H^8O^4)}}$$

6th. As yet, only the neutral bialcoholic and acid monoalcoholic ethers have been obtained with tartaric acid. It is probable that several other kinds exist.

7th. Recently, two molecules of acetyl have been substituted for two atoms of hydrogen in bialcoholic tartaric ethers, by submitting these ethers to the action of the chloride of acetyl, which proves positively the tetratomicity of tartaric acid :

$$\underset{\text{Diethylic tartrate.}}{\left(\mathrm{C^4H^2O^{2iv}}\left\{\begin{matrix}\mathrm{OC^2H^5}\\ \mathrm{OC^2H^5}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\right.\right)} + 2\underset{\substack{\text{Chloride of}\\ \text{acetyl.}}}{\left(\left.\begin{matrix}\mathrm{C^2H^3O}\\ \mathrm{Cl}\end{matrix}\right\}\right)} = 2\underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\text{Diaceto-diethylic tartrate.}}{\left(\mathrm{C^4H^2O^{2iv}}\left\{\begin{matrix}\mathrm{OC^2H^5}\\ \mathrm{OC^2H^5}\\ \mathrm{OC^2H^3O}\\ \mathrm{OC^2H^3O}\end{matrix}\right.\right)}$$

8th. Calcined with caustic potash, tartaric acid splits up into potassic oxalate and acetate:

$$\underset{\text{Tartaric acid.}}{(C^4H^6O^6)} = \underset{\text{Oxalic acid.}}{(C^2H^2O^4)} + \underset{\text{Acetic acid.}}{(C^2H^4O^2)}$$

9th. When tartaric acid is acted on by a mixture of monohydrated nitric acid and sulphuric acid, it is transformed into a product of nitrous substitution, called nitrotartaric acid, and which, when left to spontaneous decomposition at a temperature not exceeding 30°, gives a new acid—tartronic acid—which appears to be the inferior homologue of malic acid, having for formula ($C^3H^4O^5$).

An acid ($C^5H^8O^6$) which Kékulé has obtained by causing moist oxide of silver to act on bibromo-pyrotartaric acid, has not as yet been studied.

**Citric Acid** ($C^6H^8O^7$).—Citric acid is extracted from the juice of the lemon. This juice is slightly fermented to separate any mucilaginous matters, then it is saturated when hot, by chalk. It will be found advantageous to finish the saturation with quicklime. A precipitate of citrate of calcium is formed, which is washed, using warm water, as this precipitate dissolves in cold water. It is then decomposed by dilute sulphuric acid, the sulphate of calcium produced is separated by filtration, and the citric acid is crystallized. Up to the present time citric acid has not been obtained synthetically.

Properties.—1st. Citric acid crystallizes in rhombic prisms terminated by four trapezoidal faces. It is colourless, inodorous, and has a very acid taste. It dissolves in three-fourths of its weight of cold water, and half its weight of boiling water. Alcohol also dissolves it; its crystals contain a molecule of water of crystallization, which they lose at 100°.

2nd. Citric acid precipitates baryta, but not lime; but the solution of citrate of calcium deposits the greater part of this salt on boiling.

3rd. Citric acid is tetratomic. On desiccating the basic citrate of copper $\left(\left.\begin{matrix}(C^6H^4O^{3\text{iv}})^2\\ H^2Cu^3\end{matrix}\right\}O^8, \left.\begin{matrix}Cu''\\ H^2\end{matrix}\right\}O^2 + \text{aq.}\right)$, this salt loses two molecules of water besides its water of crystallization, and there is formed two molecules of citrate $\left(\left.\begin{matrix}(C^6H^4O^3)^{\text{IV}}\\ Cu^2\end{matrix}\right\}{}^4\right)$, in which $Cu^2$ takes the place of $H^4$.

4th. Citric acid is tribasic; with alkaline metals it can give three series of salts: the first neutral and trimetallic $\left(\left.\begin{matrix}C^6H^4O^3\\ H\,M'^3\end{matrix}\right\}O^4\right)$, the second bimetallic and monoacid $\left(\left.\begin{matrix}C^6H^4O^3\\ H.M'^2H\end{matrix}\right\}O^4\right)$, and the last monometallic and biacid $\left(\left.\begin{matrix}C^6H^4O^3\\ H.M'H^2\end{matrix}\right\}O^4\right)$. Three series of citric ethers are known which correspond to these three series of salts.

5th. There also exist citric ethers in which $H^3$ being replaced by radicles of alcohol, a fourth atom of hydrogen is replaced by acetyl. These ethers, obtained like the analogous tartaric ethers, demonstrate that citric acid is tetratomic.

6th. Citric acid, submitted to the action of heat, first loses $H^2O$, and gives aconitic acid :

$$\underset{\text{Citric acid.}}{\left(\left.\begin{matrix}C^6H^4O^{3\text{iv}}\\ H^4\end{matrix}\right\}O^4\right)} = \underset{\text{Water.}}{\left.\begin{matrix}H\\ H\end{matrix}\right\}O} + \underset{\text{Aconitic acid.}}{\left(\left.\begin{matrix}C^6H^3O^{3'''}\\ H^3\end{matrix}\right\}O^3\right)}$$

This latter body cannot be considered as a citric anhydride ; such an anhydride would be biatomic, while aconitic acid has a basicity equal to three. It must therefore be admitted that the water eliminated is formed half at the expense of the radicle, and half at that of the typical hydrogen.

7th. When the action of heat on aconitic acid is continued, carbonic anhydride is disengaged, and a new acid—itaconic acid—is produced :

$$\underset{\text{Aconitic acid.}}{\left(\left.\begin{matrix}C^6H^3O^{3'''}\\ H^3\end{matrix}\right\}O^3\right)} = \underset{\substack{\text{Carbonic}\\ \text{anhydride.}}}{(CO^2)} + \underset{\text{Itaconic acid.}}{\left(\left.\begin{matrix}C^5H^4O^{2''}\\ H^2\end{matrix}\right\}O^2\right)}$$

When still greater heat is applied, the itaconic acid loses water and gives anhydrous pyrocitric acid ($C^5H^4O^3$). When this is dissolved in water it regains the molecule of water it had lost; but instead of returning to the state of itaconic acid, it gives an isomer of this body—citraconic acid.

Finally, under the influence of hydriodic or nitric acid, citraconic acid is transformed into a third isomer, mesaconic acid. We have spoken elsewhere of itaconic, mesaconic, and citraconic acids (*see* Non-Saturated Biatomic and Bibasic Acids).

7th. Melted with hydrate of potassium, citric acid is transformed into oxalate and acetate :

$$\underset{\text{Citric acid.}}{(C^6H^8O^7)} + \underset{\text{Water.}}{(H^2O)} = \underset{\text{Oxalic acid.}}{(C^2H^2O^4)} + \underset{\text{Acetic acid.}}{2\,(C^2H^4O^2)}$$

## PENTATOMIC ACIDS.

None are as yet known.

In the first edition it was said that citric acid, although classed among tetratomic acids, might nevertheless possibly be pentatomic. This possibility can no longer be admitted, as M. Wislicenus has in this acid replaced 3H by ethyl, and 1H by acetyl, but has not been able to substitute acetyl for a fifth atom of H.

## HEXATOMIC ACIDS.

One hexatomic and monobasic acid is known — mannitic acid $(C^6H^{12}O^7) = \left(\left.\begin{matrix}C^6H^6O^{\text{vi}}\\ H^6\end{matrix}\right\}O^6\right)$, and two hexatomic and bibasic isomeric acids—mucic and saccharic acids $(C^6H^{10}O^8) = \left(\left.\begin{matrix}C^6H^4O^{2\text{vi}}\\ H^6\end{matrix}\right\}O^6\right)$. Mannitic acid has been obtained by Gorup-Bésanez, by oxidizing mannite by means of platinum black.

Saccharic acid is obtained by oxidizing mannite, cane-sugar, glucose, etc., by nitric acid. Mucic acid is prepared by oxidizing lactose, galactose, dulcite, and the gums in the same manner.

The hexatomic nature of saccharic acid cannot be doubted, as a saccharate of lead has been obtained in which $H^6$ is replaced by $Pb^3$.

## AMIDES.

Amides are to acids what compound ammonias are to alcohols; they are bodies which result from the replacement of the hydrogen of ammonia by an acid radicle. In studying amides we will follow the same method as we employed in the study of compound ammonias, and consider successively the amides which correspond to mono, bi, tri, etc., atomic acids.

## AMIDES DERIVED FROM MONATOMIC ACIDS.

Monatomic acids may be regarded as containing the residue OH united to a monatomic radicle. They can only therefore lose the group OH once, and consequently can only give rise to a single residue, which is always monatomic.

Monatomic acid radicles may be substituted for one, two, or three atoms of the hydrogen of ammonia, and thus produce

$$\text{primary } \left.\begin{matrix}R\\ H\\ H\end{matrix}\right\}N,\ \text{secondary } \left.\begin{matrix}R\\ R\\ H\end{matrix}\right\}N,\ \text{and tertiary } \left.\begin{matrix}R\\ R\\ R\end{matrix}\right\}N$$

amides.

Compounds belonging to the ammonium type, and containing four acid radicles, are never obtained: there are no amides corresponding to the quaternary ammonias.

Preparation of Primary Amides.—These bodies may be obtained by four different processes.

1st. By heating an ammoniacal salt; a molecule of water is set free and an amide remains. The ammonium loses $H^2$, which unite with the typical oxygen of the salt to form water, and there remains therefore the group $NH^2$; that is to say ammonia less an atom of hydrogen, and a monatomic radicle, which takes the place of this hydrogen:

$$\underset{\text{Acetate of ammonium.}}{\left(\left.\begin{matrix}C^2H^3O\\ NH^4\end{matrix}\right\}O\right)} = \underset{\text{Water.}}{\left.\begin{matrix}H\\ H\end{matrix}\right\}O} + \underset{\text{Acetamide.}}{\left(\left.\begin{matrix}C^2H^3O\\ H\\ H\end{matrix}\right\}N\right)}$$

2nd. When a compound ether is treated with ammonia, an amide and alcohol are produced. This reaction is more or less easy; sometimes it requires the assistance of heat, and sometimes it takes place at the ordinary temperature:

$$\underset{\text{Benzoate of ethyl.}}{\left(\left.\begin{matrix}C^7H^5O\\ C^2H^5\end{matrix}\right\}O\right)} + \underset{\text{Ammonia.}}{\left(\left.\begin{matrix}H\\ H\\ H\end{matrix}\right\}N\right)} = \underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\ H\end{matrix}\right\}O\right)} + \underset{\text{Benzamide.}}{\left(\left.\begin{matrix}C^7H^5O\\ H\\ H\end{matrix}\right\}N\right)}$$

3rd. Ammoniacal gas is made to act on an acid chloride; chloride of ammonium and an amide are produced:

$$\underset{\text{Chloride of butyryl.}}{\left(\left.\begin{matrix}C^4H^7O\\ Cl\end{matrix}\right\}\right)} + \underset{\text{Ammonia.}}{2\left(\left.\begin{matrix}H\\ H\\ H\end{matrix}\right\}N\right)} = \underset{\text{Chloride of ammonium.}}{\left(\left.\begin{matrix}NH^4\\ Cl\end{matrix}\right\}\right)} + \underset{\text{Butyramide.}}{\left(\left.\begin{matrix}C^4H^7O\\ H\\ H\end{matrix}\right\}N\right)}$$

4th. An acid anhydride is submitted to the action of ammonia; an amide and an ammoniacal salt are formed:

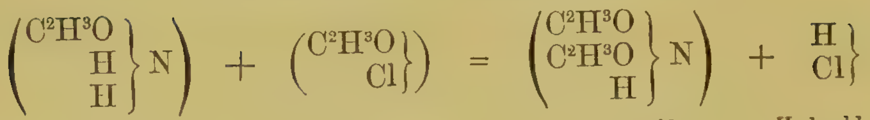
$$\underset{\text{Valeric anhydride.}}{\left(\left.\begin{matrix}C^5H^9O\\ C^5H^9O\end{matrix}\right\}O\right)} + \underset{\text{Ammonia.}}{2\left(\left.\begin{matrix}H\\ H\\ H\end{matrix}\right\}N\right)} = \underset{\text{Valerate of ammonium.}}{\left(\left.\begin{matrix}C^5H^9O\\ NH^4\end{matrix}\right\}O\right)} + \underset{\text{Valeramide.}}{\left(\left.\begin{matrix}C^5H^9O\\ H\\ H\end{matrix}\right\}N\right)}$$

In these different reactions, when ethylated, methylated, phenylated, etc. ammonias are substituted for ordinary ammonia, amides are obtained in which one or both the remaining atoms of hydrogen are also replaced by alcohol radicles.

Thus on heating benzoate of aniline, phenyl-benzamide or benzanilide is obtained:

$$\underset{\text{Benzoate of aniline.}}{\left(\left.\begin{matrix}C^7H^5O\\ NH^3(C^6H^5)\end{matrix}\right\}O\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)} + \underset{\text{Phenyl-benzamide or benzanilide.}}{\left(\left.\begin{matrix}C^7H^5O\\ C^6H^5\\ H\end{matrix}\right\}N\right)}$$

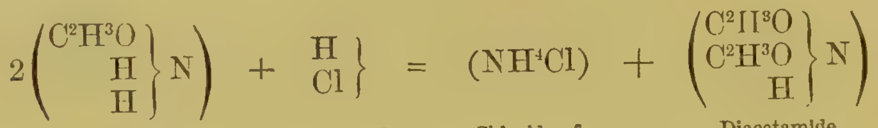
Preparation of Secondary and Tertiary Amides. — Secondary amides are obtained:—1st, by causing acid chlorides to react with the primary amides;



$$\left(\left.\begin{matrix}C^2H^3O\\H\\H\end{matrix}\right\}N\right) + \left(\left.\begin{matrix}C^2H^3O\\Cl\end{matrix}\right\}\right) = \left(\left.\begin{matrix}C^2H^3O\\C^2H^3O\\H\end{matrix}\right\}N\right) + \left.\begin{matrix}H\\Cl\end{matrix}\right\}$$

Acetamide. Chloride of acetyl. Diacetamide. Hydrochloric acid.

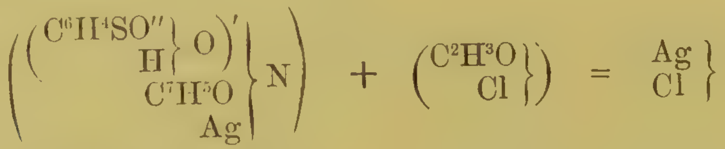
2nd. By the action of hydrochloric acid on the primary amides at a high temperature:



$$2\left(\left.\begin{matrix}C^2H^3O\\H\\H\end{matrix}\right\}N\right) + \left.\begin{matrix}H\\Cl\end{matrix}\right\} = (NH^4Cl) + \left(\left.\begin{matrix}C^2H^3O\\C^2H^3O\\H\end{matrix}\right\}N\right)$$

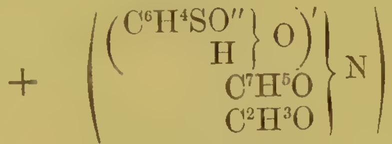
Acetamide. Hydrochloric acid. Chloride of ammonium. Diacetamide.

Gerhardt has obtained tertiary amides, by treating the salts of secondary amides with acid chlorides:



$$\left(\left.\begin{matrix}\left(\left.\begin{matrix}C^6H^4SO''\\H\end{matrix}\right\}O\right)'\\C^7H^5O\\Ag\end{matrix}\right\}N\right) + \left(\left.\begin{matrix}C^2H^3O\\Cl\end{matrix}\right\}\right) = \left.\begin{matrix}Ag\\Cl\end{matrix}\right\}$$

Nitride of silver, benzoyl, and sulphophenyl. Chloride of acetyl. Chloride of silver.

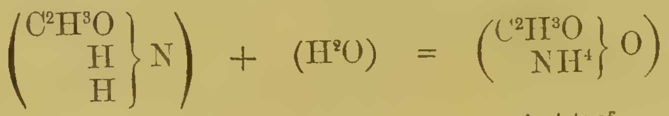


$$+ \left(\left.\begin{matrix}\left(\left.\begin{matrix}C^6H^4SO''\\H\end{matrix}\right\}O\right)'\\C^7H^5O\\C^2H^3O\end{matrix}\right\}N\right)$$

Nitride of acetyl, benzoyl, and sulphophenyl.

Properties.—The properties of the primary and secondary monamides only are well known.

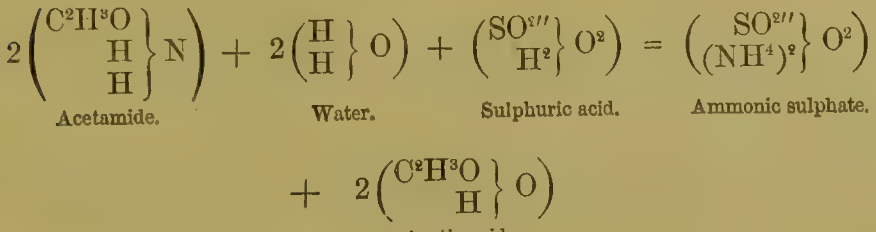
*Properties of Primary Monamides.*—1st. When heated with water in a hermetically-sealed tube, at a temperature of about 200°, these amides absorb a molecule of water, and are transformed into the ammoniacal salt of the acid the radicle of which they contain:



$$\left(\left.\begin{matrix}C^2H^3O\\H\\H\end{matrix}\right\}N\right) + (H^2O) = \left(\left.\begin{matrix}C^2H^3O\\NH^4\end{matrix}\right\}O\right)$$

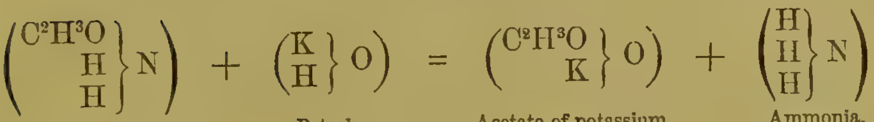
Acetamide. Water. Acetate of ammonium.

The same reaction takes place when amides are heated with hydrating agents, such as alkaline bases or dilute mineral acids. Only in this case, instead of ammonium, there are obtained the products of its decomposition by the reagents employed. Thus, if acetamide be heated with sulphuric acid, ammonic sulphate and acetic acid are produced; if the same body be treated with potash, acetate of potassium and ammonia are formed:



$$2\left(\left.\begin{matrix}C^2H^3O\\H\\H\end{matrix}\right\}N\right)+2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)+\left(\left.\begin{matrix}SO^{2\prime\prime}\\H^2\end{matrix}\right\}O^2\right)=\left(\left.\begin{matrix}SO^{2\prime\prime}\\(NH^4)^2\end{matrix}\right\}O^2\right)+2\left(\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O\right)$$

Acetamide. Water. Sulphuric acid. Ammonic sulphate. Acetic acid.

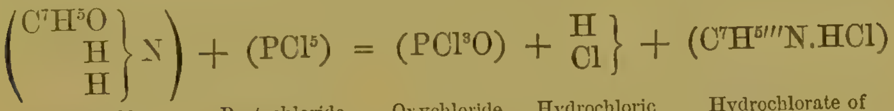


$$\left(\left.\begin{matrix}C^2H^3O\\H\\H\end{matrix}\right\}N\right)+\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)=\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right)+\left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right)$$

Acetamide. Potash. Acetate of potassium. Ammonia.

2nd. Submitted to the action of acid chlorides, the amides lose hydrochloric acid and give rise to secondary amides; acted upon by hydriodic ethers, they produce hydriodic acid and a mixed ammonia containing both an acid and an alcohol radicle.

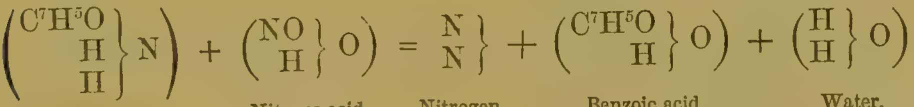
3rd. Treated with pentachloride of phosphorus, they give a chloride, which may be considered as the hydrochlorate of the nitryle corresponding to the amide employed; oxychloride of phosphorus and hydrochloric acid are formed at the same time:



$$\left(\left.\begin{matrix}C^7H^5O\\H\\H\end{matrix}\right\}N\right)+(PCl^5)=(PCl^3O)+\left.\begin{matrix}H\\Cl\end{matrix}\right\}+(C^7H^{5\prime\prime\prime}N.HCl)$$

Benzamide. Pentachloride of phosphorus. Oxychloride of phosphorus. Hydrochloric acid. Hydrochlorate of benzonitryle.

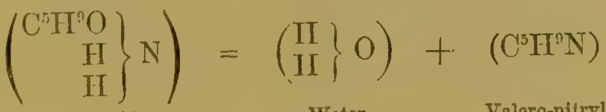
4th. Nitrous acid transforms the primary amides into nitrogen, water, and the acid of the radicle contained in the amide:



$$\left(\left.\begin{matrix}C^7H^5O\\H\\H\end{matrix}\right\}N\right)+\left(\left.\begin{matrix}NO\\H\end{matrix}\right\}O\right)=\left.\begin{matrix}N\\N\end{matrix}\right\}+\left(\left.\begin{matrix}C^7H^5O\\H\end{matrix}\right\}O\right)+\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

Benzamide. Nitrous acid. Nitrogen. Benzoic acid. Water.

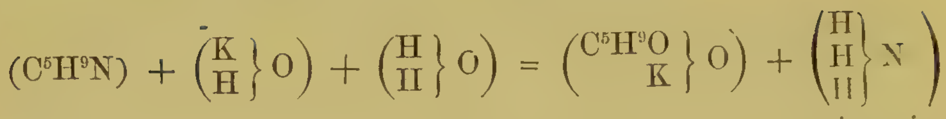
5th. When strongly heated with dehydrating bodies, such as phosphoric anhydride, these amides lose a molecule of water and give new compounds, which are called nitryles:



$$\left(\left.\begin{matrix}C^5H^9O\\H\\H\end{matrix}\right\}N\right)=\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)+(C^5H^9N)$$

Valeramide. Water. Valero-nitryle.

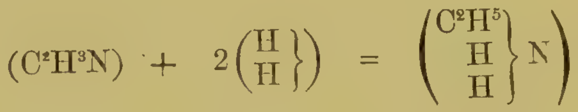
When these nitryles are submitted to the influence of hydrating agents, they absorb two molecules of water, and give the same ammoniacal salt as would be furnished by their original amide if it were hydrated. If the hydrating agents employed be bases or acids, instead of an ammoniacal salt, products of its decomposition are obtained:



$$(C^5H^9N) + \left(\begin{matrix}K\\H\end{matrix}\Big\}O\right) + \left(\begin{matrix}H\\H\end{matrix}\Big\}O\right) = \left(\begin{matrix}C^5H^9O\\K\end{matrix}\Big\}O\right) + \left(\begin{matrix}H\\H\\H\end{matrix}\Bigg\}N\right)$$

Valeronitryle. Potash. Water. Potassic valerate. Ammonia.

Submitted to the influence of nascent hydrogen, each nitryle absorbs $H^4$, and is transformed into the primary compound ammonia of the alcohol corresponding to the acid whence it is derived:



$$(C^2H^3N) + 2\left(\begin{matrix}H\\H\end{matrix}\Big\}\right) = \left(\begin{matrix}C^2H^5\\H\\H\end{matrix}\Bigg\}N\right)$$

Acetonitryle. Hydrogen. Ethylamine.

The nitryle derived from a given acid has the same composition as the hydrocyanic ether of the lower series. Thus aceto-nitryle ($C^2H^3N$) has the same composition as the cyanide of methyl $\left(\begin{matrix}CH^3\\CN\end{matrix}\Big\}\right)$. Are these bodies identical? They were long believed to be, and really are so in the series of fatty acids, but it is doubtful whether they are in the aromatic series. It is probable that, by hydration, the nitryles would reproduce the same acids as were used to prepare them. Thus Cannizzaro has shown that the hydrocyanic ethers of this series, acted on by alkalies, give, not the acid homologous with that which corresponds to the alcohol whence they are derived, but an isomer of this acid. There is therefore reason to think that the isomerism observed between the acids continues, and that in the aromatic series the nitryles are not identical with the hydrocyanic ethers, unless the nitryles derived from benzoic acid and its homologues be the hydrocyanic ethers of the phenols (*see* Phenols), while the nitryles of isomers of the homologues of benzoic acid would be the hydrocyanic ethers of the true aromatic alcohols (as is very probable).

The nitryles combine directly with hydrochloric, hydrobromic, and hydriodic acids, as is shown by Gauthier's experiments. The most important reactions of the nitryles would lead us to regard these bodies as tertiary monamines, in which a triatomic radicle would be substituted for $H^3$. Thus acetonitryle would be $C^2H^{3'''}N$. This hypothesis accounts for the formation of nitryles by means of ammoniacal salts, for the action of hydrating agents upon them, for the basic characters which they manifest, and for the manner in which they act in presence of nascent hydrogen.

When $2(H^2O)$ is taken away from an ammoniacal salt, the $H^4$ is taken from the ammonium, and the $O^2$ from the halogen residue of the acid. These latter consist of an atom of typical oxygen which was attached to carbon by a single atomicity, and of an atom of oxygen joined to the carbon by both its atomicities; the halogen residue, thus deprived of its two O from being monatomic, becomes triatomic—

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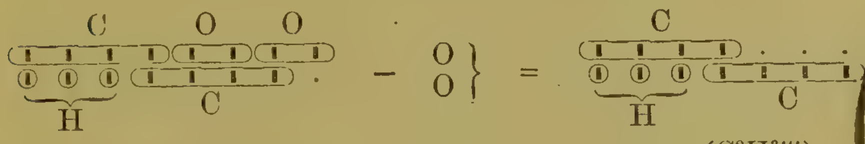


Oxacetyl $(C^2H^3O^{2\prime})$. − Oxygen. = Vinyl $(C^2H^{3\prime\prime\prime})$,

and saturates the nitrogen which remains from the ammonium:

$$\left(\left.\begin{matrix}C^2H^3O\\NH^4\end{matrix}\right\}O\right) = 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + (C^2H^{3\prime\prime\prime}N)$$

Ammonic acetate. Water. Acetonitryle.

The action of hydrating agents can be explained equally well, as it is merely the reverse of the preceding. So also the transformation of the nitryles into primary monamines. The fixation of $H^2$ on a triatomic radicle renders this latter monatomic, which obliges the nitrogen again to absorb $H^2$ to be saturated:

$$(C^2H^{3\prime\prime\prime}N) + 2(H^2) = \left(\left.\begin{matrix}(C^2H^3+H^2)'\\H\\H\end{matrix}\right\}N\right)$$

Acetonitryle. Hydrogen. Ethylamine.

Lastly, if nitryles be regarded as compound ammonias, their combination with hydracids follows as a matter of course.

*Properties of Secondary Amides.* — 1st. These readily dissolve in ammonia; they are acid, and can exchange their last atoms of hydrogen for metals. The metallic salts thus formed dissolve in ammonia, producing compounds which were regarded by Gerhardt as derived from two molecules of ammonia, but which, as they do not contain monatomic radicles, ought rather to be considered as derived from a single molecule of ammonia, in which H would be replaced by $(NH^4)$. According to this hypothesis, the two molecules would be united by the nitrogen acting in one of them as pentatomic:

$$\left(\left.\begin{matrix}\left(\left.\begin{matrix}C^6H^4SO''\\H\end{matrix}\right\}O\right)'\\C^7H^5O'\\Ag\end{matrix}\right\}N\right) + (NH^3) = \left(\left.\begin{matrix}\left(\left.\begin{matrix}C^6H^4SO''\\H\end{matrix}\right\}O\right)'\\(C^7H^5O)'\\(NH^3Ag)'\end{matrix}\right\}N\right)$$

Nitride of sulphophenyl, benzoyl, and silver. Ammonia. Nitride of sulphophenyl, benzoyl, and argento-ammonium.

2nd. According to Gerhardt, perchloride of phosphorus acts on secondary amides in the same way as on primary amides. But the product, instead of representing the combination of a nitryle with hydrochloric acid, represents its combination with a chloride of the acid radicle:

$$\left(\left.\begin{matrix}\left(\left.\begin{matrix}C^6H^4SO''\\H\end{matrix}\right\}O\right)'\\C^7H^5O\\H\end{matrix}\right\}N\right) + (PCl^5) = (PCl^3O) + \left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)$$

Sulphophenylamide. Perchloride of phosphorus. Oxychloride of phosphorus. Hydrochloric acid.

$$+ (C^7H^{5\prime\prime\prime}N.C^6H^4SO.HO,Cl)$$

Chloride of sulphophenyl-benzamidyl.

This chloride is decomposed by heat into an acid chloride and a nitryle.

## AMIDES OF BIATOMIC ACIDS.

The amides of monobasic and those of bibasic biatomic acids must be mentioned separately.

### AMIDES OF MONOBASIC BIATOMIC ACIDS.

These acids may give rise to three classes of amides :

1st. They may give primary, secondary, and tertiary diamides, by the substitution of their radicle for one, two, or three atoms of H in a double molecule of ammonia ;

2nd. On losing OH they leave a monatomic residue, which may be substituted for one, two, or three atoms of H in the simple type ($NH^3$), and give primary, secondary, or tertiary monamides. Moreover, these acids contain an atom of acid hydrogen and an atom of alcoholic hydrogen, and according as it is the one or the other of these atoms of hydrogen which is eliminated in the group OH, the residue is neutral or acid ; the result is that the amides containing this residue would themselves be sometimes neutral, sometimes acid. It can therefore be established that three classes of amides correspond to the acids of this group :

1st. Primary, secondary, and tertiary diamides;

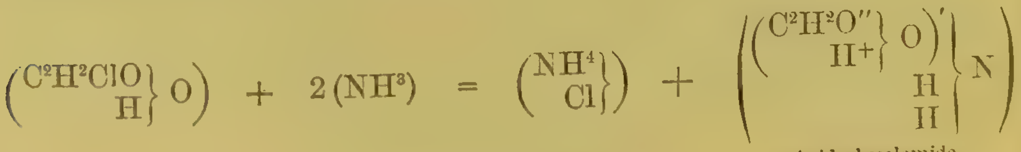
2nd. Primary, secondary, and tertiary acid monamides ;

3rd. Primary, secondary, and tertiary neutral monamides, isomeric with the preceding.

The typical hydrogen of acid amides may be replaced by radicles of alcohols. When the ethers of this nature contain the radicle ethyl, they are called amethanes.

The diamides of these acids are not yet known ; nor have the secondary and tertiary neutral monamides as yet been prepared. Only primary, secondary, and tertiary acid amides, primary neutral amides, and the ethers of acid amides are known.

**Primary Acid Monamides.**—PREPARATION.—*First Process.*—These amides are obtained by submitting the monobrominated or monochlorinated derivatives of monatomic acids of the same series to the action of ammonia. Thus acid glycolamide is obtained by means of chloracetic acid and ammonia, and acid oxybutyramide by means of ammonia and bromo-butyric acid :



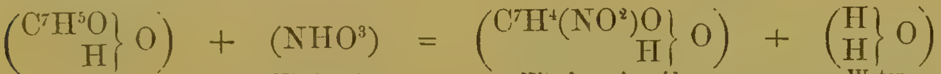
$$\left(\left.\begin{matrix}C^2H^2ClO\\H\end{matrix}\right\}O\right) + 2(NH^3) = \left(\left.\begin{matrix}NH^4\\Cl\end{matrix}\right\}\right) + \left(\left.\begin{matrix}\left(\left.\begin{matrix}C^2H^2O''\\H+\end{matrix}\right\}O\right)'\\H\\H\end{matrix}\right\}N\right)$$

Chloracetic acid. Ammonia. Ammonic chloride. Acid glycolamide.

*Second Process.*—These amides may also be prepared by combining the aldehyds with ammonia, mixing the products thus obtained with hydrocyanic acid, and submitting the mixture to the action of hydrochloric acid. This process is only applicable in the series of fatty acids, the only one in which the aldehyds can combine directly with ammonia. There is obtained in these reactions the amide of an acid which belongs to the series higher by a term than that the aldehyd of which has been taken. Thus, with ordinary aldehyd ($C^2H^4O$), which belongs to the series of which the fundamental hydrocarbide is the hydride of ethyl ($C^2H^6$), acid lactamide is formed. This belongs to the series, the fundamental hydrocarbide of which is the hydride of propyl ($C^3H^8$), the superior homologue of the hydride of ethyl:

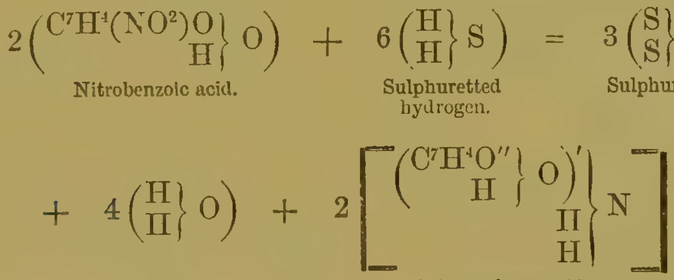
$$\underset{\text{Acetic aldehyd.}}{(C^2H^4O)} + \underset{\text{Hydrocyanic acid.}}{(CNH)} + \underset{\text{Water.}}{(H^2O)} = \underset{\text{Acid lactamide.}}{(C^3H^7NO^2)}$$

*Third Process.*—In the aromatic series, these bodies may also be prepared by reducing mononitrated monatomic acids by hydrosulphuric acid. These acids result from the action of fuming nitric acid on the monatomic acids themselves:



$$\left(\left.\begin{matrix}C^7H^5O\\ H\end{matrix}\right\}O\right) + (NHO^3) = \left(\left.\begin{matrix}C^7H^4(NO^2)O\\ H\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)$$

Benzoic acid. Nitric acid. Nitrobenzoic acid. Water.



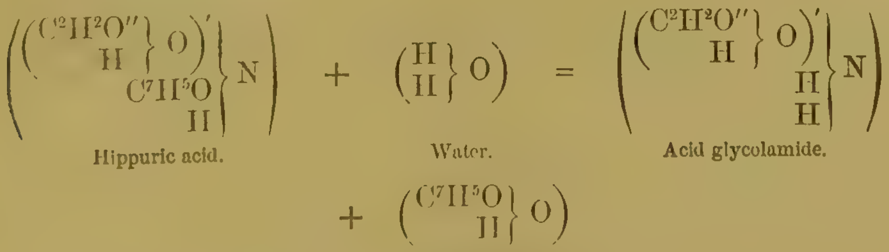
$$2\left(\left.\begin{matrix}C^7H^4(NO^2)O\\ H\end{matrix}\right\}O\right) + 6\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}S\right) = 3\left(\left.\begin{matrix}S\\ S\end{matrix}\right\}\right)$$

Nitrobenzoic acid. Sulphuretted hydrogen. Sulphur.

$$+ 4\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right) + 2\left[\left.\begin{matrix}\left(\left.\begin{matrix}C^7H^4O''\\ H\end{matrix}\right\}O\right)'\\ H\\ H\end{matrix}\right\}N\right]$$

Water. Acid oxybenzamide.

*Fourth Process.*—Acid glycolamide is produced in the hydration of certain bodies which exist ready formed in animal secretions. These bodies are mixed amides, which contain, besides the radicle ($C^2H^3O^2$), the radicle of another acid. Hydrating agents divide them into this acid and acid glycolamide:



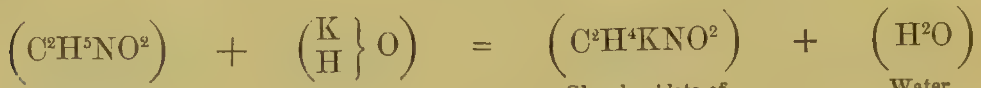
$$\left(\left.\begin{matrix}\left(\left.\begin{matrix}C^2H^2O''\\ H\end{matrix}\right\}O\right)'\\ C^7H^5O\\ H\end{matrix}\right\}N\right) + \left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}\left(\left.\begin{matrix}C^2H^2O''\\ H\end{matrix}\right\}O\right)'\\ H\\ H\end{matrix}\right\}N\right)$$

Hippuric acid. Water. Acid glycolamide.

$$+ \left(\left.\begin{matrix}C^7H^5O\\ H\end{matrix}\right\}O\right)$$

Benzoic acid.

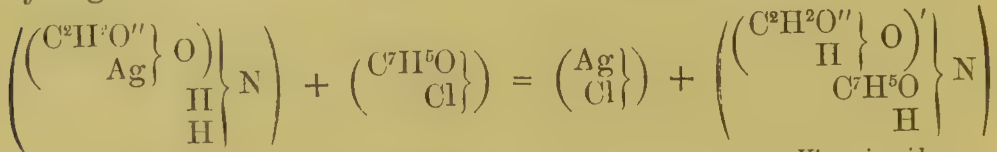
PROPERTIES.—1st. These monamides may act like acids or like ammonia. If they are made to act on bases, they exchange H for a metal and give well-defined salts; if they are made to act on an acid, they combine with it directly, like ammonia, and also produce well-defined salts, capable of forming a great number of double salts with metallic salts:



$$\underset{\text{Acid glycolamide (glycocol).}}{(C^2H^5NO^2)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Glycolamidate of potassium.}}{(C^2H^4KNO^2)} + \underset{\text{Water.}}{(H^2O)}$$

$$\underset{\text{Glycocol.}}{(C^2H^5NO^2)} + \underset{\text{Hydrochloric acid.}}{(HCl)} = \underset{\text{Hydrochlorate of glycocol.}}{(C^2H^5NO^2,HCl)}$$

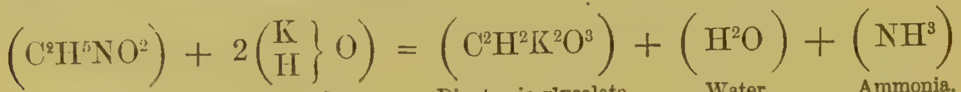
2nd. The argentic salts of these amides, acted on by the chloride of an acid radicle, furnish chloride of silver, and a secondary amide resulting from the substitution of the acid radicle for a second atom of hydrogen:



$$\underset{\text{Glycolamidate of silver.}}{\left(\left.\begin{matrix}\left(\left.\begin{matrix}C^2H^2O''\\Ag\end{matrix}\right\}O\right)\\H\\H\end{matrix}\right\}N\right)} + \underset{\text{Chloride of benzoyl.}}{\left(\left.\begin{matrix}C^7H^5O\\Cl\end{matrix}\right\}\right)} = \underset{\text{Chloride of silver.}}{\left(\left.\begin{matrix}Ag\\Cl\end{matrix}\right\}\right)} + \underset{\text{Hippuric acid.}}{\left(\left.\begin{matrix}\left(\left.\begin{matrix}C^2H^2O''\\H\end{matrix}\right\}O\right)'\\C^7H^5O\\H\end{matrix}\right\}N\right)}$$

All the animal compounds which give glycocol when hydrated, have a constitution analogous to that of hippuric acid.

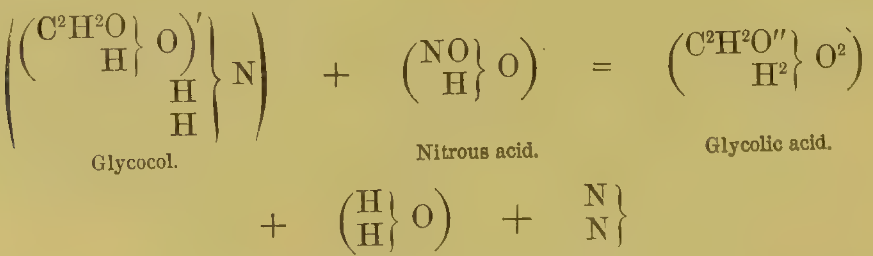
3rd. Alkalies never transform the amides of this class into alkaline salts of their corresponding acid and ammonia. Such a reaction would produce a bimetallic salt, as the following equation indicates—



$$\underset{\text{Glycocol.}}{(C^2H^5NO^2)} + 2\underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Dipotassic glycolate.}}{(C^2H^2K^2O^3)} + \underset{\text{Water.}}{(H^2O)} + \underset{\text{Ammonia.}}{(NH^3)}$$

which is impossible, as the acids whence these amides are derived are only monobasic.

4th. Submitted to the action of nitrous acid, these amides disengage nitrogen, water is liberated, and the acid to which the amide corresponds is also set free:



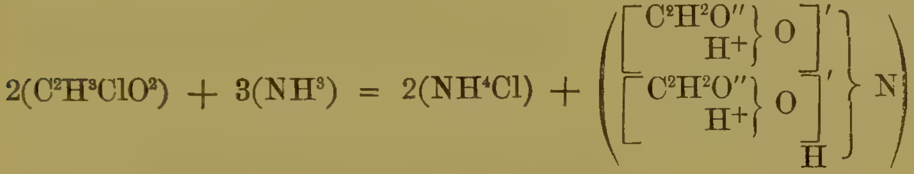
$$\underset{\text{Glycocol.}}{\left(\left.\begin{matrix}\left(\left.\begin{matrix}C^2H^2O\\H\end{matrix}\right\}O\right)'\\H\\H\end{matrix}\right\}N\right)} + \underset{\text{Nitrous acid.}}{\left(\left.\begin{matrix}NO\\H\end{matrix}\right\}O\right)} = \underset{\text{Glycolic acid.}}{\left(\left.\begin{matrix}C^2H^2O''\\H^2\end{matrix}\right\}O^2\right)}$$

$$+ \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Nitrogen.}}{\left.\begin{matrix}N\\N\end{matrix}\right\}}$$

5th. The action of dehydrating agents has not been examined, but from analogy it may be supposed that these bodies are capable of losing a molecule of water and of being transformed into monamides, in which $H^2$ would be replaced by a biatomic acid radicle. In fact, such bodies do exist in other series, and are called imides.

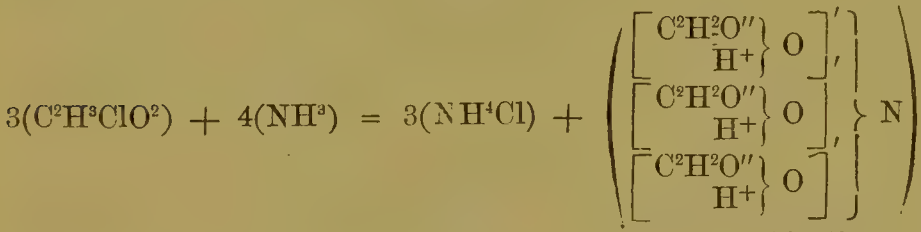
**Secondary and Tertiary Acid Monamides.** — These bodies have been little studied; we only know, from the researches of M. Heintz, that they are produced at the same time as primary monamides when these are prepared by the first process described. These amides naturally contain a number of atoms of basic hydrogen equal to the number of atoms of the residue introduced into the molecule; secondary amides are therefore bibasic, and tertiary amides tribasic.

The mode of formation of these compounds is explained by the following equations:



$$2(C^2H^3ClO^2) + 3(NH^3) = 2(NH^4Cl) + \left(\left.\begin{array}{l}\left[\left.\begin{array}{r}C^2H^2O''\\ H+\end{array}\right\}O\right]'\\ \left[\left.\begin{array}{r}C^2H^2O''\\ H+\end{array}\right\}O\right]'\\ \quad\quad\quad H\end{array}\right\}N\right)$$

Chloracetic acid. Ammonia. Chloride of ammonium. Diglycolamidic acid.



$$3(C^2H^3ClO^2) + 4(NH^3) = 3(NH^4Cl) + \left(\left.\begin{array}{l}\left[\left.\begin{array}{r}C^2H^2O''\\ H+\end{array}\right\}O\right]'\\ \left[\left.\begin{array}{r}C^2H^2O''\\ H+\end{array}\right\}O\right]'\\ \left[\left.\begin{array}{r}C^2H^2O''\\ H+\end{array}\right\}O\right]'\end{array}\right\}N\right)$$

Chloracetic acid. Ammonia. Chloride of ammonium. Triglycolamidic acid.

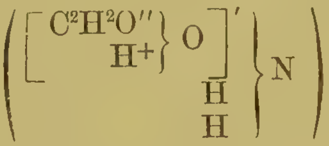
NOMENCLATURE AND ENUMERATION OF THE COMPOUNDS KNOWN IN THIS GROUP.—Until recently, no regular nomenclature has been attempted for these bodies; their names were formed by merely adding the termination *amic* to the names of the monatomic acids of the same series. It is upon this principle that glycocol ($C^2H^5NO^2$) has been called acetamic acid; that the analogous compound of the benzoic series is called benzamic acid, etc.

It is evident that this nomenclature must be relinquished, for it connects these compounds with monatomic acids, while they are really biatomic. Recently, M. Heintz has proposed to name these bodies by adding the termination *amidic* to the name of the biatomic acid the elements of which they contain. On placing the sylables *mono*, *di*, or *tri*, before this name, we indicate whether the amide is of the first, second, or third degree; the prefix *mono* may be suppressed. According to this system, the three amides derived from glycolic acid are called: glycol amidic, diglycol amidic, and triglycolamidic acid; the acid amide derived from lactic acid is lactamidic acid, etc. We shall adopt this nomenclature.

The bodies actually known in this group are the following:

1st. In the series of the acids $C^nH^{2n}O^3$:

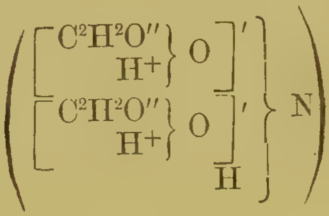
Glycolamidic acid . .



$$\left(\left.\begin{matrix}\left[\left.\begin{matrix}C^2H^2O''\\H+\end{matrix}\right\}O\right]'\\H\\H\end{matrix}\right\}N\right)$$

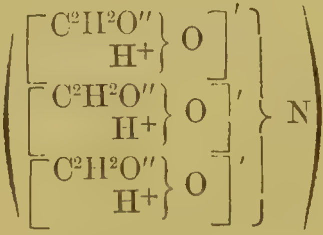
SYNONYMS. GLYCOCOL, SUGAR OF GELATINE, ACETAMIC ACID.

Diglycolamidic acid .



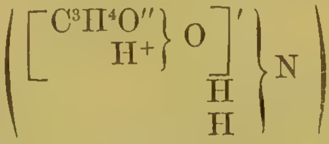
$$\left(\left.\begin{matrix}\left[\left.\begin{matrix}C^2H^2O''\\H+\end{matrix}\right\}O\right]'\\\left[\left.\begin{matrix}C^2H^2O''\\H+\end{matrix}\right\}O\right]'\\H\end{matrix}\right\}N\right)$$

Triglycolamidic acid .



$$\left(\left.\begin{matrix}\left[\left.\begin{matrix}C^2H^2O''\\H+\end{matrix}\right\}O\right]'\\\left[\left.\begin{matrix}C^2H^2O''\\H+\end{matrix}\right\}O\right]'\\\left[\left.\begin{matrix}C^2H^2O''\\H+\end{matrix}\right\}O\right]'\end{matrix}\right\}N\right)$$

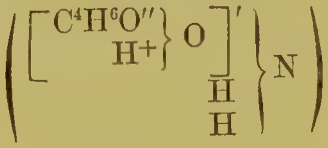
Lactamidic acid . .



$$\left(\left.\begin{matrix}\left[\left.\begin{matrix}C^3H^4O''\\H+\end{matrix}\right\}O\right]'\\H\\H\end{matrix}\right\}N\right)$$

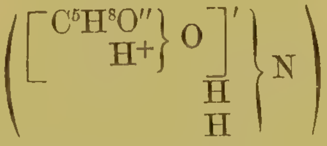
ALANINE.

Oxybutyramidic acid .



$$\left(\left.\begin{matrix}\left[\left.\begin{matrix}C^4H^6O''\\H+\end{matrix}\right\}O\right]'\\H\\H\end{matrix}\right\}N\right)$$

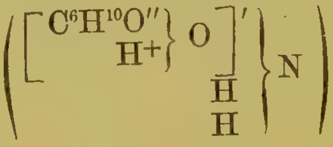
Oxyvaleramidic acid .



$$\left(\left.\begin{matrix}\left[\left.\begin{matrix}C^5H^8O''\\H+\end{matrix}\right\}O\right]'\\H\\H\end{matrix}\right\}N\right)$$

AMIDO-VALERIC ACID.

Oxycaproamidic acid .

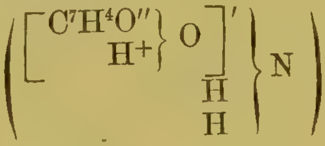


$$\left(\left.\begin{matrix}\left[\left.\begin{matrix}C^6H^{10}O''\\H+\end{matrix}\right\}O\right]'\\H\\H\end{matrix}\right\}N\right)$$

LEUCINE.

2nd. In the series of the acids $C^nH^{2n-8}O^3$:

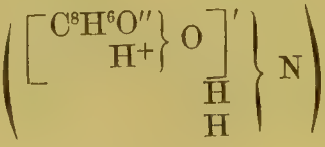
Oxybenzamidic acid .



$$\left(\left.\begin{matrix}\left[\left.\begin{matrix}C^7H^4O''\\H+\end{matrix}\right\}O\right]'\\H\\H\end{matrix}\right\}N\right)$$

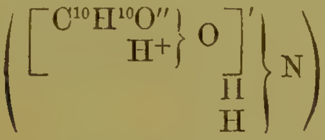
BENZAMIC ACID, AMIDO-BENZOIC ACID.

Oxytoluamidic acid .



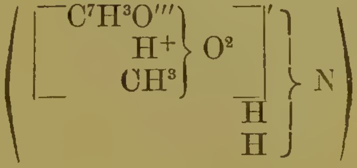
$$\left(\left.\begin{matrix}\left[\left.\begin{matrix}C^8H^6O''\\H+\end{matrix}\right\}O\right]'\\H\\H\end{matrix}\right\}N\right)$$

TOLUAMIC ACID, AMIDO-TOLUIC ACID.

Oxycuminamidic acid 

$$\left(\left.\begin{array}{r}\left[\left.\begin{array}{r}C^{10}H^{10}O''\\ H+\end{array}\right\}O\right]'\\ H\\ H\end{array}\right\}N\right)$$

CUMINAMIC ACID, AMIDO-CUMINIC ACID.

Oxyanisamidic acid . 

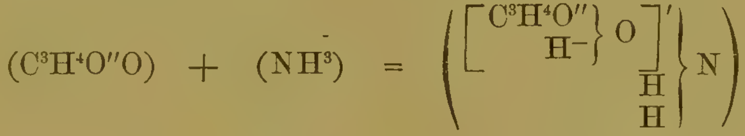
$$\left(\left.\begin{array}{r}\left[\left.\begin{array}{r}C^{7}H^{3}O'''\\ H+\\ CH^{3}\end{array}\right\}O^{2}\right]'\\ H\\ H\end{array}\right\}N\right)$$

ANISAMIC ACID.

Glycolamidic acid has been called sugar of gelatine because it has a sweet taste, and is produced when gelatine is submitted to the action of the alkalies or of sulphuric acid.

Leucine is found in the animal economy, and especially in the pancreas.

**Neutral Monamides.**—These are very little known, lactamide alone having been at all studied. It is obtained by the action of lactic anhydride on ammonia:



$$(C^{3}H^{4}O''O) \quad + \quad (NH^{3}) \quad = \quad \left(\left.\begin{array}{r}\left[\left.\begin{array}{r}C^{3}H^{4}O''\\ H-\end{array}\right\}O\right]'\\ H\\ H\end{array}\right\}N\right)$$

Lactic anhydride. Ammonia. Neutral lactamide.

When lactic amide reacts with the caustic alkalies, they form alkaline lactate and ammonia:

$$(C^{3}H^{7}NO^{2}) \quad + \quad (KHO) \quad = \quad (C^{3}H^{5}KO^{3}) \quad + \quad (NH^{3})$$

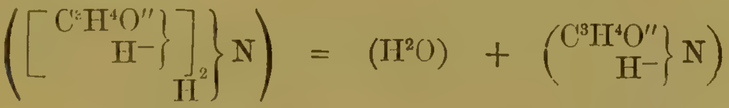
Neutral lactamide. Potash. Potassic lactate. Ammonia.

Nitrous acid transforms it into lactic acid, nitrogen, and water:

$$(C^{3}H^{7}NO^{2}) \quad + \quad (NHO^{2}) \quad = \quad (H^{2}O) \quad + \quad N^{2} \quad + \quad (C^{3}H^{6}O^{3})$$

Lactamide. Nitrous acid. Water. Nitrogen. Lactic acid.

It is not known how dehydrating agents would act on lactamide; probably it would lose $(H^{2}O)$, and produce a neutral amide, according to the equation:

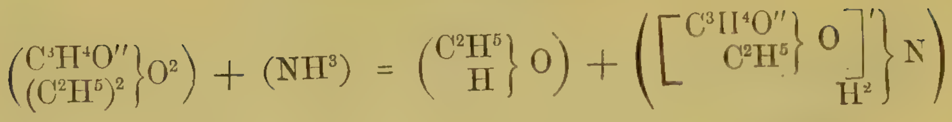


$$\left(\left.\begin{array}{r}\left[\left.\begin{array}{r}C^{3}H^{4}O''\\ H-\end{array}\right\}\right]_{2}\\ H\end{array}\right\}N\right) \quad = \quad (H^{2}O) \quad + \quad \left(\left.\begin{array}{r}C^{3}H^{4}O''\\ H-\end{array}\right\}N\right)$$

Lactamide. Water. Lactimide?

**Ethers of Acid Amides.**—These ethers may be obtained:

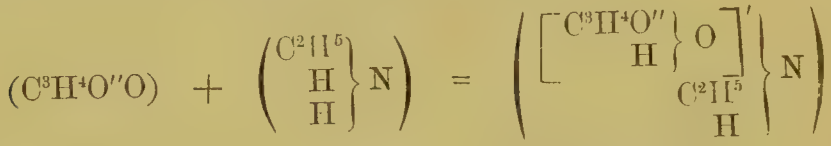
1st. By treating diethylic ethers of non-amidated acids by an alcoholic solution of ammonia:



$$\left(\left.\begin{matrix}C^3H^4O''\\(C^2H^5)^2\end{matrix}\right\}O^2\right) + (NH^3) = \left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}\left[\left.\begin{matrix}C^3H^4O''\\C^2H^5\end{matrix}\right\}O\right]'\\H^2\end{matrix}\right\}N\right)$$

Diethylic lactate. Ammonia. Alcohol. Lactamethane.

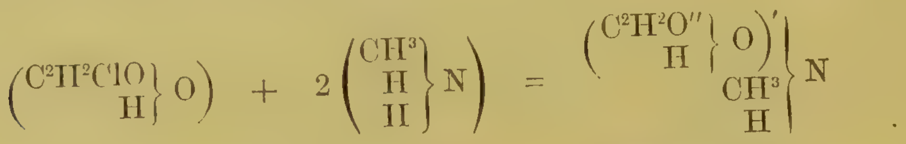
2nd. By submitting the anhydrides of non-amidated acids to the action of a primary monamine:



$$(C^3H^4O''O) + \left(\left.\begin{matrix}C^2H^5\\H\\H\end{matrix}\right\}N\right) = \left(\left.\begin{matrix}\left[\left.\begin{matrix}C^3H^4O''\\H\end{matrix}\right\}O\right]'\\C^2H^5\\H\end{matrix}\right\}N\right)$$

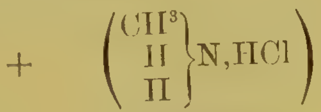
Lactic anhydride. Ethylamine. Lactethylamide.

3rd. By causing a primary monamine to act on a monochlorinated or monobrominated monatomic acid:



$$\left(\left.\begin{matrix}C^2H^2ClO\\H\end{matrix}\right\}O\right) + 2\left(\left.\begin{matrix}CH^3\\H\\H\end{matrix}\right\}N\right) = \left.\begin{matrix}\left(\left.\begin{matrix}C^2H^2O''\\H\end{matrix}\right\}O\right)'\\CH^3\\H\end{matrix}\right\}N$$

Chloracetic acid. Methylamine. Methyl-glycolamide.

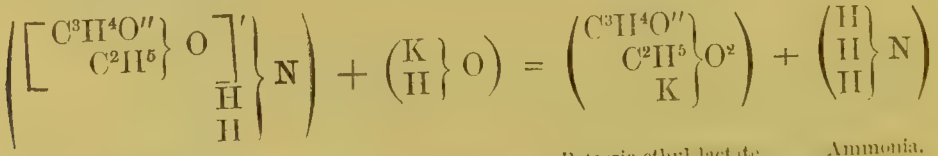


$$+ \left(\left.\begin{matrix}CH^3\\H\\H\end{matrix}\right\}N,HCl\right)$$

Hydrochlorate of methylamine.

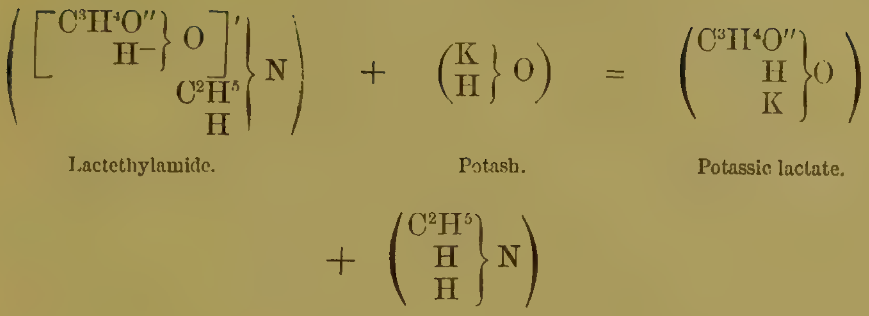
Properties.—In the same series, the compounds obtained by these different processes have the same empirical formulæ, but they are not identical. At least it is certain that there is a difference between the products prepared by the first process and those prepared by the second.

While the lactamethane resulting from the action of ammonia on dialcoholic ethers is decomposed, under the influence of alkalies, into ethyl-lactate and ammonia, that obtained by the reaction of ethylamine with lactic anhydride is decomposed under the same conditions into ethylamine and lactate. This isomerism may be expressed in rational formulæ by supposing that, in lactamethane, the ethyl is substituted for the typical hydrogen of the residue of lactic acid, while in lactethylamide this same ethyl is directly substituted for the hydrogen of the ammonia. The preceding reactions may then be easily explained, as is shown by the following equations:



$$\left(\left.\begin{matrix}\left[\left.\begin{matrix}C^3H^4O''\\C^2H^5\end{matrix}\right\}O\right]'\\H\\H\end{matrix}\right\}N\right) + \left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}C^3H^4O''\\C^2H^5\\K\end{matrix}\right\}O^2\right) + \left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right)$$

Lactamethane. Potash. Potassic ethyl-lactate. Ammonia.



$$\left(\left.\begin{matrix}\left[\left.\begin{matrix}C^3H^4O'' \\ H-\end{matrix}\right\}O\right]' \\ C^2H^5 \\ H\end{matrix}\right\}N\right) + \left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}C^3H^4O''\\H\\K\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}C^2H^5\\H\\H\end{matrix}\right\}N\right)$$

Lactethylamide. Potash. Potassic lactate. Ethylamine.

There is reason to suppose that the body obtained by the third process is identical with that obtained by the second; but this is not quite certain, as these methods have never both been applied in the same series. However, methyl-glycol-amide, when heated with an alkali, disengages methylamine, as lactethylamide disengages ethylamine. This analogy in their reaction tends to prove the identity of the products prepared by the two methods.

Methyl-glycol-amide is isomeric with lactamide. Before its nature was known, its formation by the division of creatine had been observed, and it was called sarcosine:

$$\underset{\text{Creatine.}}{(C^4H^9N^3O^2)} + \underset{\text{Water.}}{(H^2O)} = \underset{\text{Urea.}}{(CH^4N^2O)} + \underset{\text{Sarcosine.}}{(C^3H^7NO^2)}$$

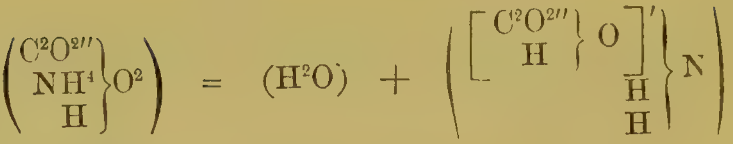
## AMIDES OF BIATOMIC AND BIBASIC ACIDS.

The biatomic radicle of these acids may be substituted for two, four, or six atoms of hydrogen in the type of two atoms of ammonia condensed. It may also be substituted for $H^2$ in the simple ammonia type; thence arise primary, secondary, and tertiary diamides, and monamides containing a biatomic radicle: these latter are called imides. In the second place, a biatomic and bibasic acid may, on losing OH, give rise to a monatomic residue, which, when substituted for H, $H^2$, or $H^3$ in a simple ammonia, would give a primary, secondary, or tertiary monamide.

**Monamides.**—In the bibasic acids the two atoms of typical hydrogen are both strongly basic. Whichever may be the atom eliminated in the group OH, that which remains always possesses basic properties. Consequently the monatomic residue is always the same, and its substitution for the hydrogen of ammonia can only give rise to a single series of amides instead of producing two series of isomeric amides, as we have seen is the case with biatomic monobasic acids.

Only the primary amides of this order are known.

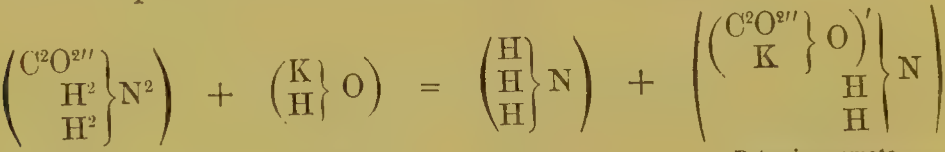
Preparation.—*First Process.*—These amides are obtained by carefully distilling an acid ammoniacal salt:



$$\left(\left.\begin{array}{l}C^2O^{2\prime\prime}\\ NH^4\\ H\end{array}\right\}O^2\right) = (H^2O) + \left(\left.\begin{array}{l}\left[\left.\begin{array}{l}C^2O^{2\prime\prime}\\ H\end{array}\right\}O\right]'\\ H\\ H\end{array}\right\}N\right)$$

Acid oxalate of ammonium. Water. Oxamic acid.

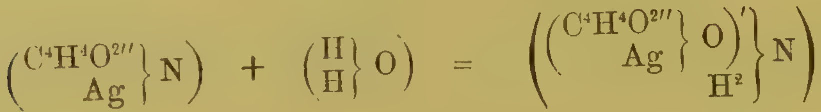
*Second Process.*—They are also obtained by decomposing the diamides by half the quantity of alkali necessary to produce complete decomposition:



$$\left(\left.\begin{array}{l}C^2O^{2\prime\prime}\\ H^2\\ H^2\end{array}\right\}N^2\right) + \left(\left.\begin{array}{l}K\\ H\end{array}\right\}O\right) = \left(\left.\begin{array}{l}H\\ H\\ H\end{array}\right\}N\right) + \left(\left.\begin{array}{l}\left(\left.\begin{array}{l}C^2O^{2\prime\prime}\\ K\end{array}\right\}O\right)'\\ H\\ H\end{array}\right\}N\right)$$

Oxamide. Potash. Ammonia. Potassic oxamate.

*Third Process.*—An imide is boiled in water:

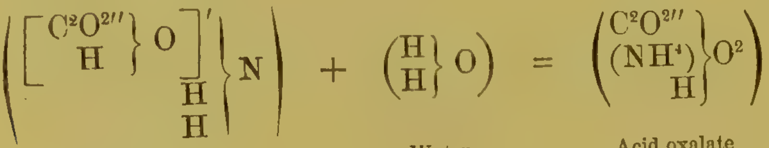


$$\left(\left.\begin{array}{l}C^4H^4O^{2\prime\prime}\\ Ag\end{array}\right\}N\right) + \left(\left.\begin{array}{l}H\\ H\end{array}\right\}O\right) = \left(\left.\begin{array}{l}\left(\left.\begin{array}{l}C^4H^4O^{2\prime\prime}\\ Ag\end{array}\right\}O\right)'\\ H^2\end{array}\right\}N\right)$$

Argentic succinimide. Water. Succinamate of silver.

PROPERTIES.—1st. The monamides of this class all act as monatomic acids.

2nd. As they only differ from an acid ammoniacal salt by the elements of a molecule of water, they can be transformed into such a salt by the action of hydrating agents:

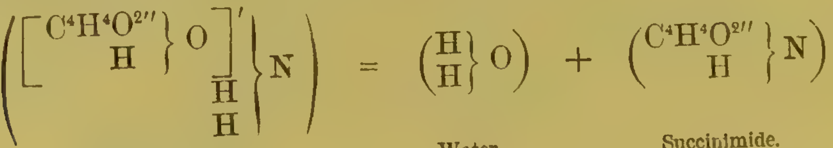


$$\left(\left.\begin{array}{l}\left[\left.\begin{array}{l}C^2O^{2\prime\prime}\\ H\end{array}\right\}O\right]'\\ H\\ H\end{array}\right\}N\right) + \left(\left.\begin{array}{l}H\\ H\end{array}\right\}O\right) = \left(\left.\begin{array}{l}C^2O^{2\prime\prime}\\ (NH^4)\\ H\end{array}\right\}O^2\right)$$

Oxamic acid. Water. Acid oxalate of ammonium.

When the hydrating agent used is an acid or an alkali, instead of an acid salt of ammonia, the products of its decomposition are obtained.

3rd. Dehydrating agents, such as anhydrous phosphoric acid, cause these bodies to lose water and transform them into imides:



$$\left(\left.\begin{array}{l}\left[\left.\begin{array}{l}C^4H^4O^{2\prime\prime}\\ H\end{array}\right\}O\right]'\\ H\\ H\end{array}\right\}N\right) = \left(\left.\begin{array}{l}H\\ H\end{array}\right\}O\right) + \left(\left.\begin{array}{l}C^4H^4O^{2\prime\prime}\\ H\end{array}\right\}N\right)$$

Succinamic acid. Water. Succinimide.

4th. Added to the solutions of these amides, nitrous acid causes a disengagement of nitrogen, a molecule of water is eliminated, and the acid of which the amide contains the elements is produced:

$$\underset{\text{Oxamic acid.}}{\left(\left.\begin{array}{r}\left[\left.\begin{array}{c}C^2O^{2\prime\prime}\\H\end{array}\right\}O\right]^{\prime}\\H\\H\end{array}\right\}N\right)} + \underset{\text{Nitrous acid.}}{\left(\left.\begin{array}{c}NO\\H\end{array}\right\}O\right)} = \underset{\text{Water.}}{\left(\left.\begin{array}{c}H\\H\end{array}\right\}O\right)} + \underset{\text{Nitrogen.}}{\left.\begin{array}{c}N\\N\end{array}\right\}}$$

$$+ \underset{\text{Oxalic acid.}}{\left(\left.\begin{array}{c}C^2O^{2\prime\prime}\\H^2\end{array}\right\}O^2\right)}$$

Nomenclature.—These bodies are named by replacing the termination of the name of the acid by *amic.* Thus we say oxamic acid, succinamic acid, etc.

**Diamides.**—Only primary diamides have as yet been prepared.

Preparation.—*First Process.*—A neutral salt of ammonium is submitted to careful distillation :

$$\underset{\text{Neutral oxalate of ammonium.}}{\left(\left.\begin{array}{c}C^2O^{2\prime\prime}\\(NH^4)^2\end{array}\right\}O^2\right)} = 2\underset{\text{Water.}}{\left(\left.\begin{array}{c}H\\H\end{array}\right\}O\right)} + \underset{\text{Oxamide.}}{\left(\left.\begin{array}{c}C^2O^{2\prime\prime}\\H^2\\H^2\end{array}\right\}N^2\right)}$$

*Second Process.*—A neutral ether is treated with aqueous ammonia, and a diamide and an alcohol are produced :

$$\underset{\text{Diethylic succinate.}}{\left(\left.\begin{array}{c}C^4H^4O^{2\prime\prime}\\(C^2H^5)^2\end{array}\right\}O^2\right)} + 2\underset{\text{Ammonia.}}{\left(\left.\begin{array}{c}H\\H\\H\end{array}\right\}N\right)} = \underset{\text{Succinamide.}}{\left(\left.\begin{array}{c}C^4H^4O^{2\prime\prime}\\H^2\\H^2\end{array}\right\}N^2\right)} + 2\underset{\text{Alcohol.}}{\left(\left.\begin{array}{c}C^2H^5\\H\end{array}\right\}O\right)}$$

*Third Process.*—A chloride of an acid radicle is made to act on dry ammoniacal gas :

$$\underset{\text{Chloride of an acid radicle.}}{\left(\left.\begin{array}{c}R^{\prime\prime}\\Cl^2\end{array}\right\}\right)} + 4\underset{\text{Ammonia.}}{\left(\left.\begin{array}{c}H\\H\\H\end{array}\right\}N\right)} = 2\underset{\text{Ammonic chloride.}}{\left(\left.\begin{array}{c}NH^4\\Cl\end{array}\right\}\right)} + \underset{\text{Diamide.}}{\left(\left.\begin{array}{c}R^{\prime\prime}\\H^2\\H^2\end{array}\right\}N^2\right)}$$

These three processes are identical with the three first spoken of under the primary monamides derived from monatomic acids.

*Fourth Process.*—By the action of ammonia on imides :

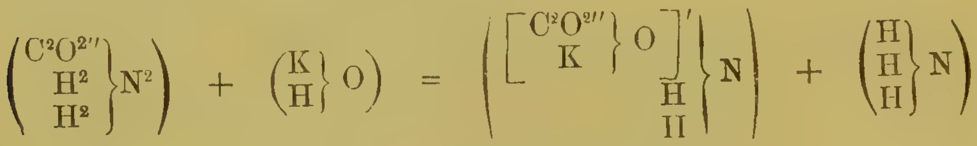
$$\underset{\text{Imide.}}{\left(\left.\begin{array}{c}R^{\prime\prime}\\H\end{array}\right\}N\right)} + \underset{\text{Ammonia.}}{\left(\left.\begin{array}{c}H\\H\\H\end{array}\right\}N\right)} = \underset{\text{Diamide.}}{\left(\left.\begin{array}{c}R^{\prime\prime}\\H^2\\H^2\end{array}\right\}N^2\right)}$$

Properties.—1st. These amides can absorb water and be transformed into neutral ammoniacal salts :

$$\underset{\text{Oxamide.}}{\left(\left.\begin{array}{c}C^2O^{2\prime\prime}\\H^2\\H^2\end{array}\right\}N^2\right)} + 2\underset{\text{Water.}}{\left(\left.\begin{array}{c}H\\H\end{array}\right\}O\right)} = \underset{\text{Neutral oxalate of ammonium.}}{\left(\left.\begin{array}{c}C^2O^{2\prime\prime}\\(NH^4)^2\end{array}\right\}O^2\right)}$$

If an acid or an alkali be used for the hydration, the products of the decomposition of the ammoniacal salt by these agents are obtained.

2nd. When treated by half the quantity of base necessary to effect their complete decomposition, these bodies give ammonia and the alkaline salt of an acid amide:

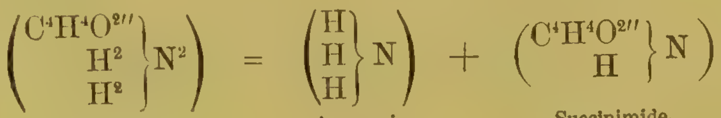


$$\left(\left.\begin{matrix}C^2O^{2\prime\prime}\\H^2\\H^2\end{matrix}\right\}N^2\right) + \left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}\left[\left.\begin{matrix}C^2O^{2\prime\prime}\\K\end{matrix}\right\}O\right]'\\H\\H\end{matrix}\right\}N\right) + \left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right)$$

Oxamide. Potash. Potassic oxamate. Ammonia.

3rd. It is probable that under the influence of dehydrating agents, these amides would lose two molecules of water and be transformed into nitryles, identical or isomeric with the hydrocyanic ethers of glycols lower by two terms in the series. It has been seen that when an alkali acts on the dicyanhydrin of a glycol, a biatomic and bibasic acid is obtained, belonging to a series higher by two terms than that of the glycol whose dicyanhydrin was employed. However, the direct dehydration of the diamides has not as yet been effected.

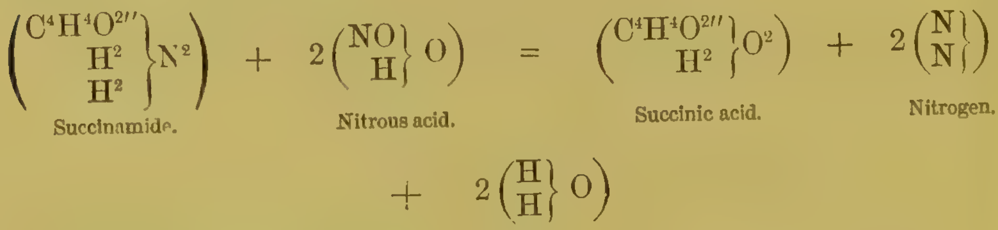
4th. When heated alone the diamides lose ammonia, and are transformed into imides:



$$\left(\left.\begin{matrix}C^4H^4O^{2\prime\prime}\\H^2\\H^2\end{matrix}\right\}N^2\right) = \left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right) + \left(\left.\begin{matrix}C^4H^4O^{2\prime\prime}\\H\end{matrix}\right\}N\right)$$

Succinamide. Ammonia. Succinimide.

5th. Nitrous acid re-forms the acid whence the amide is derived; water and nitrogen are produced at the same time:

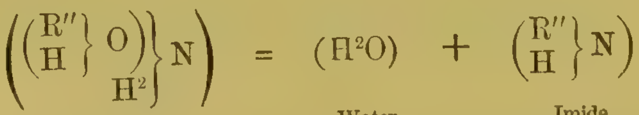


$$\left(\left.\begin{matrix}C^4H^4O^{2\prime\prime}\\H^2\\H^2\end{matrix}\right\}N^2\right) + 2\left(\left.\begin{matrix}NO\\H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}C^4H^4O^{2\prime\prime}\\H^2\end{matrix}\right\}O^2\right) + 2\left(\left.\begin{matrix}N\\N\end{matrix}\right\}\right) + 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

Succinamide. Nitrous acid. Succinic acid. Nitrogen. Water.

**Imides.**—PREPARATION.—*First Process.*—Imides are obtained by decomposing diamides by heat.

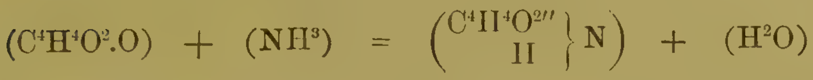
*Second Process.*—They are also obtained by dehydrating acid amides:



$$\left(\left.\begin{matrix}\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)\\H^2\end{matrix}\right\}N\right) = (H^2O) + \left(\left.\begin{matrix}R''\\H\end{matrix}\right\}N\right)$$

Acid amide. Water. Imide.

*Third Process.*—Imides may also be prepared by causing ammonia to act on an anhydrous biatomic and bibasic acid:

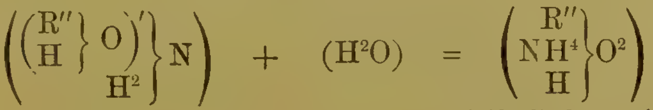


$$(C^4H^4O^2.O) + (NH^3) = \left(\left.\begin{matrix}C^4H^4O^{2''}\\H\end{matrix}\right\}N\right) + (H^2O)$$

Succinic anhydride. Ammonia. Succinimide. Water.

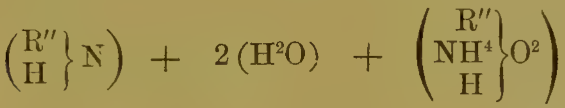
PROPERTIES.—1st. The imides always act as monobasic acids.

2nd. Under the influence of hydrating agents, imides give the same products as acid amides. But to do this they absorb twice the quantity of water:



$$\left(\left.\begin{matrix}\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)'\\H^2\end{matrix}\right\}N\right) + (H^2O) = \left(\left.\begin{matrix}R''\\NH^4\\H\end{matrix}\right\}O^2\right)$$

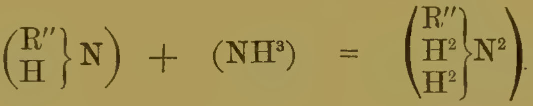
Acid amide. Water. Acid salt of ammonium.



$$\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}N\right) + 2(H^2O) + \left(\left.\begin{matrix}R''\\NH^4\\H\end{matrix}\right\}O^2\right)$$

Imide. Water. Acid salt of ammonium.

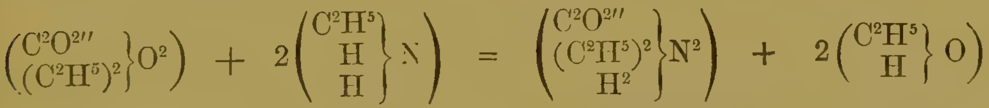
3rd. It is probable that, under suitable conditions, the imides could absorb ammonia and be transformed into diamides:



$$\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}N\right) + (NH^3) = \left(\left.\begin{matrix}R''\\H^2\\H^2\end{matrix}\right\}N^2\right).$$

Imide. Ammonia. Diamide.*

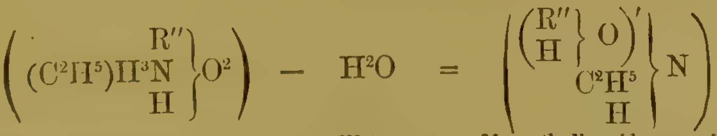
**Amides containing Alcohol Radicles.**—In the preparation of diamides, if a compound ammonia be substituted for ordinary ammonia, amides are obtained which contain the radicles of alcohols:



$$\left(\left.\begin{matrix}C^2O^{2''}\\(C^2H^5)^2\end{matrix}\right\}O^2\right) + 2\left(\left.\begin{matrix}C^2H^5\\H\\H\end{matrix}\right\}N\right) = \left(\left.\begin{matrix}C^2O^{2''}\\(C^2H^5)^2\\H^2\end{matrix}\right\}N^2\right) + 2\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)$$

Oxalate of ethyl. Ethylamine. Diethyl-oxamide. Alcohol.

So also on substituting primary monamides for ammonia in the preparation of acid monamides, the acid monamides obtained contain alcohol radicles:



$$\left(\left.\begin{matrix}R''\\(C^2H^5)H^3N\\H\end{matrix}\right\}O^2\right) - H^2O = \left(\left.\begin{matrix}\left(\left.\begin{matrix}R''\\H\end{matrix}\right\}O\right)'\\C^2H^5\\H\end{matrix}\right\}N\right)$$

Acid salt of ethyl-ammonium. Water. Monoethylic acid monamide.

Bodies of the same composition as these latter, but neutral, are

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* Imides are derived from acid amides by the elimination of water, as nitryles are derived by elimination of water from neutral amides. Nitryles fix nascent hydrogen, giving compound ammonias. It might be supposed from analogy that nascent hydrogen would also be fixed by the imides, but M. Oppenheim and myself have ascertained that this is not the case.

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obtained when dry ammoniacal gas is made to act on a dialcoholic ether:

$$\left(\left.\begin{array}{c}C^2O^{2\prime\prime}\\(C^2H^5)^2\end{array}\right\}O^2\right) + (NH^3) = \left(\left.\begin{array}{r}\left(\left.\begin{array}{c}C^2O^{2\prime\prime}\\C^2H^5\end{array}\right\}O\right)'\\H\\H\end{array}\right\}N\right) + \left(\left.\begin{array}{c}C^2H^5\\H\end{array}\right\}O\right)$$

Oxalate of ethyl. Ammonia. Oxamethane. Alcohol.

These latter bodies decompose, under the influence of alkalies, into alkaline salts, ammonia, and alcohol:

$$\left(\left.\begin{array}{r}\left(\left.\begin{array}{c}C^2O^{2\prime\prime}\\C^2H^5\end{array}\right\}O\right)'\\H\\H\end{array}\right\}N\right) + 2\left(\left.\begin{array}{c}K\\H\end{array}\right\}O\right) = \left(\left.\begin{array}{c}C^2O^{2\prime\prime}\\K^2\end{array}\right\}O^2\right) + \left(\left.\begin{array}{c}C^2H^5\\H\end{array}\right\}O\right)$$

Oxamethane. Potash. Potassic oxalate. Alcohol.

$$+ \left(\left.\begin{array}{c}H\\H\\H\end{array}\right\}N\right)$$

Ammonia.

On the contrary, their isomers, obtained by means of compound ammonias, give compound ammonia, water, and an alkaline salt by the action of alkalies:

$$\left(\left.\begin{array}{r}\left(\left.\begin{array}{c}R''\\H\end{array}\right\}O\right)'\\C^2H^5\\H\end{array}\right\}N\right) + 2\left(\left.\begin{array}{c}K\\H\end{array}\right\}O\right) = \left(\left.\begin{array}{c}R''\\K^2\end{array}\right\}O^2\right) + \left(\left.\begin{array}{c}H\\H\end{array}\right\}O\right)$$

Monoethylic acid monamide. Potash. Neutral potassic salt. Water.

$$+ \left(\left.\begin{array}{c}C^2H^5\\H\\H\end{array}\right\}N\right)$$

Ethylamine.

The rational formulæ we have employed to represent these isomers take into account their difference of properties. They show that in the first the alcohol radicle is substituted for the typical hydrogen of the acid residue $\left(\left.\begin{array}{c}R''\\H\end{array}\right\}O\right)$, which consequently is brought back to the neutral state, while in the others this alcohol radicle is substituted for an atom of hydrogen of the ammonia.

Those bodies which contain the radicle ethyl substituted for the typical hydrogen of the acid residue are called *amethanes*.

## AMIDES DERIVED FROM ACIDS HAVING AN ATOMICITY GREATER THAN TWO.

Triatomic acids may, by successive eliminations of HO, give rise to mono, bi, or triatomic residues, which, when substituted for the simple and condensed types,

$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}H^2\\H^2\\H^2\end{matrix}\right\}N^2 \qquad \left.\begin{matrix}H^3\\H^3\\H^3\end{matrix}\right\}N^3$$

give primary, secondary, tertiary monamides, diamides, or triamides. Reasoning from analogy, it may be deduced that tetratomic acids could produce monamides, diamides, triamides, and tetramides; pentatomic acids, monamides, diamides, triamides, tetramides, and pentamides, etc.

When polyatomic acids have a basicity equal to their atomicity, as the different residues cannot present any case of isomerism, no phenomenon of this kind is observed in the amides of which they form part. The basicity of any residue is always equal to that of the acid whence it is derived, less the number of the group OH eliminated. The result is that the most condensed amide, that which contains the radicle of the acid, is neutral, while the others are acid and present basicities equal to those of the residues which enter into their formation. It will be seen from this that the most condensed amide being neutral, that of which the condensation is less by one degree is monobasic, that of which the condensation is less by two degrees, bibasic, etc.

When polyatomic acids have a basicity inferior to their atomicity, with the exception of the radicle which does not contain typical hydrogen, each residue may result from the elimination of a group OH containing a positive hydrogen or from a group OH containing a negative hydrogen. The residues therefore present cases of isomerism which naturally are also found in the amides which are derived from them.

Let us take for example, 1st, the case of a triatomic and monobasic acid; and, 2ndly, the case of a triatomic and bibasic acid. We will represent a triatomic and monobasic acid by the general formula $\left(\left.\begin{matrix}R'''\\H^+\\H^-H^-\end{matrix}\right\}O^3\right)$. The following residues may be obtained: $\alpha\left(\left.\begin{matrix}R'''\\H^-H^-\end{matrix}\right\}O^2\right)'$ monatomic and neutral, which would furnish neutral amides; $\beta\left(\left.\begin{matrix}R'''\\H^+\\H^-\end{matrix}\right\}O^2\right)'$ monatomic and monobasic, which would furnish acid and monobasic amides; $\gamma\left(\left.\begin{matrix}R'''\\H^-\end{matrix}\right\}O\right)''$ biatomic and neutral, which would give neutral diamides; $\delta\left(\left.\begin{matrix}R''\\H^+\end{matrix}\right\}O\right)''$ biatomic and monobasic, which would give monobasic diamides; $\epsilon$ $R'''$ triatomic and neutral, which would give neutral triamides.

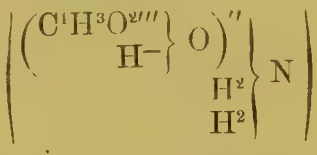
We will also represent a triatomic and bibasic acid by the general formula $\left(\left.\begin{matrix}R'''\\H^{+}H^{+}\\H^{-}\end{matrix}\right\}O^{3}\right)$ It will be seen that this acid could furnish the following residues: $\alpha$ $\left(\left.\begin{matrix}R'''\\H^{+}H^{+}\end{matrix}\right\}O^{2}\right)'$ monatomic as a radicle, and bibasic as an acid, which could produce bibasic acid monamides; $\beta$ $\left(\left.\begin{matrix}R'''\\H^{+}\\H^{-}\end{matrix}\right\}O^{2}\right)'$ monatomic as a radicle, and monobasic as an acid, which could give rise to monobasic acid monamides; $\gamma$ $\left(\left.\begin{matrix}R'''\\H^{+}\end{matrix}\right\}O\right)''$ biatomic as a radicle, and monobasic as an acid, which could give monobasic diamides; $\delta$ $\left(\left.\begin{matrix}R'''\\H^{-}\end{matrix}\right\}O\right)''$ biatomic and neutral, which could furnish neutral diamides; $\epsilon$ $R'''$ triatomic and neutral, which could give neutral triamides.

On representing by general formulæ the tetra, penta, and hexatomic acids, and exhausting in these formulæ all the combinations which can be obtained by the elimination of OH, all the amides, isomeric or not, to which they can give rise, will be easily ascertained.

However, it must be acknowledged that this is theoretical. As a matter of fact, only very few amides derived from acids having an atomicity greater than two are known.

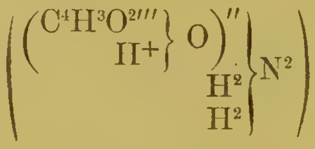
Those which are known are:

1st. The neutral malo-diamide:



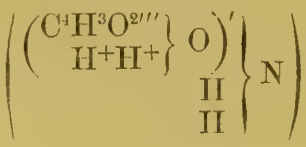
$$\left(\left.\begin{matrix}\left(\left.\begin{matrix}C^{4}H^{3}O^{2'''}\\H^{-}\end{matrix}\right\}O\right)''\\H^{2}\\H^{2}\end{matrix}\right\}N\right)$$

2nd. The acid malo-diamide known as asparagin and extracted from certain vegetables:



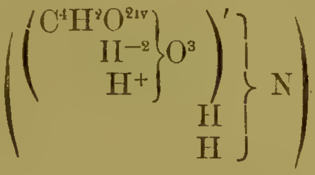
$$\left(\left.\begin{matrix}\left(\left.\begin{matrix}C^{4}H^{3}O^{2'''}\\H^{+}\end{matrix}\right\}O\right)''\\H^{2}\\H^{2}\end{matrix}\right\}N^{2}\right)$$

3rd. The bibasic malic acid monamide (aspartic acid) obtained by the action of bases on asparagin, or by the hydration of fumarimide by means of boiling hydrochloric acid:



$$\left(\left.\begin{matrix}\left(\left.\begin{matrix}C^{4}H^{3}O^{2'''}\\H^{+}H^{+}\end{matrix}\right\}O\right)'\\H\\H\end{matrix}\right\}N\right)$$

4th. Tartramic acid or tartaric acid monamide, monobasic:



$$\left(\left.\begin{array}{r}\left(\left.\begin{array}{r}C^4H^2O^{2iv}\\H^{-2}\\H^+\end{array}\right\}O^3\right)'\\H\\H\end{array}\right\}N\right)$$

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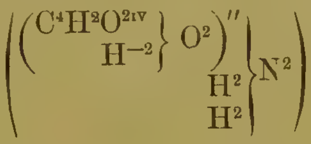
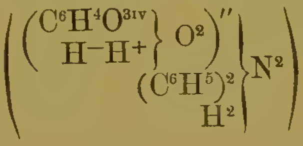
5th. Tartramide or neutral tartaric diamide:



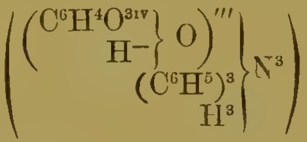
$$\left(\left.\begin{array}{r}\left(\left.\begin{array}{r}C^4H^2O^{2iv}\\H^{-2}\end{array}\right\}O^2\right)''\\H^2\\H^2\end{array}\right\}N^2\right)$$

6th. Phenyl-citrodiamic acid, or monobasic, citric acid di-phenyl-diamide:



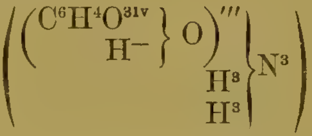
$$\left(\left.\begin{array}{r}\left(\left.\begin{array}{r}C^6H^4O^{3iv}\\H^-H^+\end{array}\right\}O^2\right)''\\(C^6H^5)^2\\H^2\end{array}\right\}N^2\right)$$

7th. Phenyl-citramide, or neutral citric phenyl-triamide:



$$\left(\left.\begin{array}{r}\left(\left.\begin{array}{r}C^6H^4O^{3iv}\\H^-\end{array}\right\}O\right)'''\\(C^6H^5)^3\\H^3\end{array}\right\}N^3\right)$$

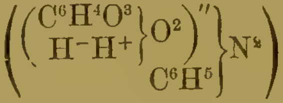
8th. Neutral citro-triamide:



$$\left(\left.\begin{array}{r}\left(\left.\begin{array}{r}C^6H^4O^{3iv}\\H^-\end{array}\right\}O\right)'''\\H^3\\H^3\end{array}\right\}N^3\right)$$

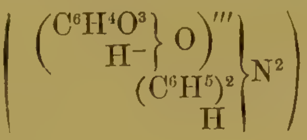
Besides these, two citric imides are known:

Phenylic monimide, which is monobasic, and which is called phenyl-citramic acid:



$$\left(\left.\begin{array}{r}\left(\left.\begin{array}{r}C^6H^4O^3\\H^-H^+\end{array}\right\}O^2\right)''\\C^6H^5\end{array}\right\}N^2\right)$$

Neutral phenylic di-imide, or phenylcitrimide:



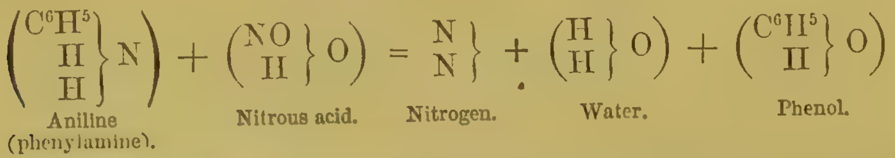
$$\left(\left.\begin{array}{r}\left(\left.\begin{array}{r}C^6H^4O^3\\H^-\end{array}\right\}O\right)'''\\(C^6H^5)^2\\H\end{array}\right\}N^2\right)$$

Several amides of polyatomic acids, such as meconic, comenic acids, etc., are known. But as the atomicity of these acids has not as yet been established, it is impossible at present to assign a satisfactory rational formula to these bodies.

## PHENOLS.

The name of phenols is given to bodies which have the same composition as the alcohols of the aromatic series, or of series which are less hydrogenized, but which in their properties present marked differences to these alcohols. All the phenols have not the same atomicity.

FORMATION OF PHENOLS.—Ordinary phenol ($C^6H^6O$) is the only one that has been produced synthetically. It may be obtained by the reaction of nitrous acid on aniline :



$$\underset{\substack{\text{Aniline}\\\text{(phenylamine).}}}{\left(\left.\begin{matrix}C^6H^5\\H\\H\end{matrix}\right\}N\right)} + \underset{\text{Nitrous acid.}}{\left(\left.\begin{matrix}NO\\H\end{matrix}\right\}O\right)} = \underset{\text{Nitrogen.}}{\left.\begin{matrix}N\\N\end{matrix}\right\}} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Phenol.}}{\left(\left.\begin{matrix}C^6H^5\\H\end{matrix}\right\}O\right)}$$

All the others are pyrogenized products derived from other organic compounds according to a law more or less regular, or they result from the splitting up of certain natural principles :

$$\underset{\text{Gallic acid.}}{(C^7H^6O^5)} = \underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{(CO^2)} + \underset{\substack{\text{Pyrogallic}\\\text{phenol.}}}{(C^6H^6O^3}$$

$$\underset{\text{Erythrin.}}{(C^{20}H^{22}O^{10})} + \underset{\text{Water.}}{2(H^2O)} = \underset{\text{Erythrite}}{(C^4H^{10}O^4)} + \underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{2(CO^2)} + \underset{\substack{\text{Orcin (biatomic}\\\text{phenol).}}}{2(C^7H^8O^2)}$$

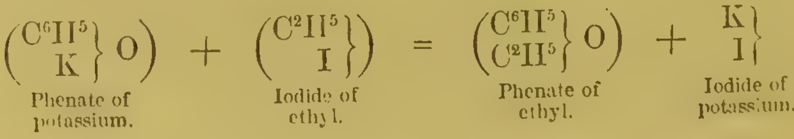
PROPERTIES.—Ordinary phenol ($C^6H^6O$) is the only one well studied : it possesses the following properties, which probably appertain to the other phenols.

1st. Phenol exchanges an atom of hydrogen for an alkaline metal by double decomposition, in presence of bases, in the same manner as acids. But the compounds thus obtained are very slightly stable, and simple distillation with water decomposes them into phenol and free base.

Carbonic anhydride, on reacting with the metallic derivatives of phenols, combines directly with them, and transforms them into the alkaline salts of acids of a higher series. The metallic derivatives of alcohols, and salts properly so called, do not appear to possess this property.

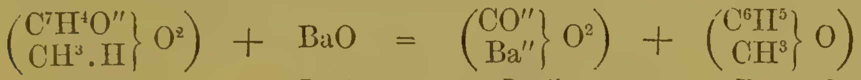
2nd. The ammoniacal compound of phenol may, on being dehydrated, be transformed into an alkaloid, aniline, the basic properties of which are very marked, though less so than those of the true alcoholic alkaloids.

3rd. On causing hydriodic ethers to react on the phenate of potassium, true mixed ethers are obtained, which contain the radicle of phenol and the radicle of an alcohol :



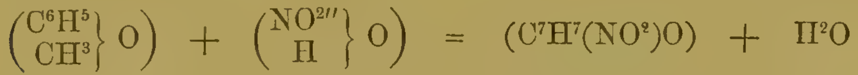
$$\underset{\substack{\text{Phenate of}\\\text{potassium.}}}{\left(\left.\begin{matrix}C^6H^5\\K\end{matrix}\right\}O\right)} + \underset{\substack{\text{Iodide of}\\\text{ethyl.}}}{\left(\left.\begin{matrix}C^2H^5\\I\end{matrix}\right\}\right)} = \underset{\substack{\text{Phenate of}\\\text{ethyl.}}}{\left(\left.\begin{matrix}C^6H^5\\C^2H^5\end{matrix}\right\}O\right)} + \underset{\substack{\text{Iodide of}\\\text{potassium.}}}{\left.\begin{matrix}K\\I\end{matrix}\right\}}$$

The same bodies may be formed in another manner: salicylic acid ($C^7H^6O^3$) is decomposed by baryta into carbonic anhydride and phenol. When the salicylate of methyl is substituted for salicylic acid in this reaction, the phenate of methyl is obtained instead of phenol:



$$\underset{\text{Monomethylic salicylate.}}{\left(\left.\begin{matrix}C^7H^4O''\\CH^3.H\end{matrix}\right\}O^2\right)} + \underset{\text{Baryta.}}{BaO} = \underset{\text{Barytic carbonate.}}{\left(\left.\begin{matrix}CO''\\Ba''\end{matrix}\right\}O^2\right)} + \underset{\text{Phenate of methyl.}}{\left(\left.\begin{matrix}C^6H^5\\CH^3\end{matrix}\right\}O\right)}$$

These ethers are never obtained by the direct action of phenol on the alcohols. They differ essentially from those which contain only radicles of alcohols and from those which contain acid radicles. While the two latter classes of ethers split up under the influence of sulphuric or nitric acids, and furnish derivatives corresponding to their two generators, the phenic ethers react with these acids, giving single derivatives analogous to those furnished by phenol itself:



$$\underset{\text{Phenate of methyl.}}{\left(\left.\begin{matrix}C^6H^5\\CH^3\end{matrix}\right\}O\right)} + \underset{\text{Nitric acid.}}{\left(\left.\begin{matrix}NO^{2''}\\H\end{matrix}\right\}O\right)} = \underset{\text{Nitrophenate of methyl.}}{(C^7H^7(NO^2)O)} + \underset{\text{Water.}}{H^2O}$$

4th. Phenols do not combine directly with acids, but, under the influence of acid chlorides, they furnish compounds which result from the substitution of an acid radicle for the hydrogen of the phenol.

These bodies, analogous by their composition either to compound ethers or to mixed anhydrides, clearly differ from both. They differ from mixed anhydrides in that water does not decompose them, and from compound ethers inasmuch as nitric acid reacts differently with several of them, especially with phosphoric phenol; and instead of being neutral like compound ethers, they appear to be, like phenol itself, capable of entering into double decomposition with bases.

5th. Phenol oxidizes with difficulty, and its oxidation takes place without loss of hydrogen, and with the formation of a product analogous to phenol. This character removes phenol from the alcohols, which in this case would lose hydrogen to give aldehyds, and then fix oxygen and be changed into acids.

6th. With phenol, chlorine gives derivatives of substitution without elimination of hydrogen; the alcohols, on the contrary, always lose two atoms of hydrogen, for which the chlorine is not substituted.

7th. Phenol when submitted to the action of nitric acid, exchanges one, two, or three atoms of hydrogen for the radicle nitryl ($NO^2$). These products, like phenol, are capable of entering into double decomposition with bases, and do not reproduce their generators under the influence of hydrating agents; alcohols, on the contrary, exchange H for $NO^2$ only once. The product is a compound ether, perfectly neutral, and capable, on becoming hydrated, of reproducing its generators.

Phenols are therefore bodies which, while having the composition of alcohols and several properties of acids, differ essentially from both these classes of bodies.

To polyatomic phenols there appear to belong a great number of colouring principles, which are either themselves phenols, as appears to be the case with alizarine ($C^{10}H^6O^3$), or are derived from them by oxidation and the fixation of ammonia:

$$\underset{\text{Orcin (biatomic phenol).}}{2(C^7H^8O^2)} + \underset{\text{Oxygen.}}{3\left(\begin{matrix}O\\O\end{matrix}\right\}\Big)} + \underset{\text{Ammonia.}}{2(NH^3)} = \underset{\text{Orcein.}}{2(C^7H^7NO^3)} + \underset{\text{Water.}}{4(H^2O)}$$

## CONSTITUTON OF PHENOLS.

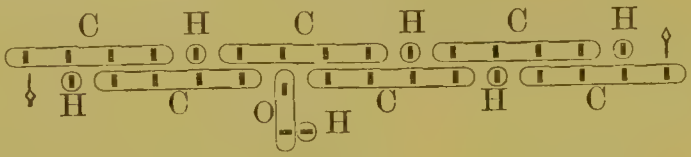
That phenols are not true alcohols is clearly shown by their properties, and it has especially become evident since, in several series, both phenols and alcohols which are isomeric with them are known. This is seen in the benzoic and in the cuminic series.

In the first of these, cresylic phenol and benzilic alcohol, both having for formula ($C^7H^8O$), and in the second thymol ($C^{10}H^{14}O$), isomeric with cuminic alcohol, are known.

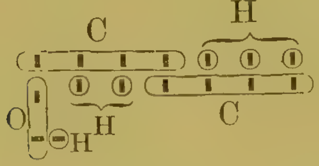
In what do these phenols differ from alcohols? Kékulé has propounded a theory which so far is in accordance with facts, and which accounts for this isomerism.

We have seen that, according to him, benzine results from the union of six atoms of carbon forming a closed chain, in which each atom loses three atomicities, only the fourth remaining free to unite with hydrogen. In this hydrocarbide, the grouping being different from that in the series $C^nH^{2n+2}$, it is evident that when OH is here substituted for H, a species of alcohol differing from the ordinary alcohols should be obtained.

Let us represent this alcoholic derivative of benzine (phenol) and ethylic alcohol by the following figures:



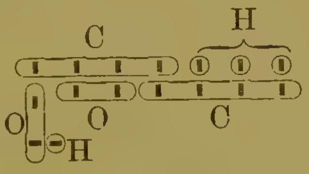
Phenol.



Ethylic alcohol.

A great difference will at once be observed in the constitution of these bodies.

In ethylic as in all alcohols, the hydroxyl OH is united to an atom of carbon, two other atomicities of which are saturated by hydrogen. The result is that this hydrogen may be exchanged for oxygen, and thus render the compound electro-negative, that is to say, transform the alcohol into an acid, as is shown by the following figure:

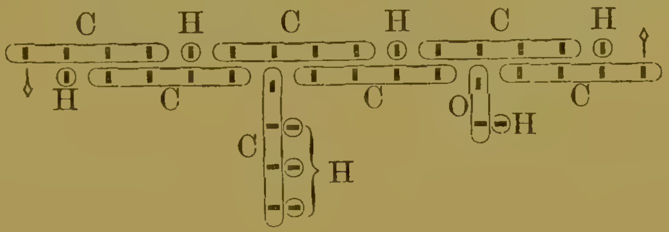


Acetic acid.

In phenol, on the contrary, the hydroxyl is united to an atom of carbon of which all the other centres of attraction are saturated by carbon; it is therefore impossible to replace $H^2$ by O near the group OH, that is to say, to transform the phenol into an acid.

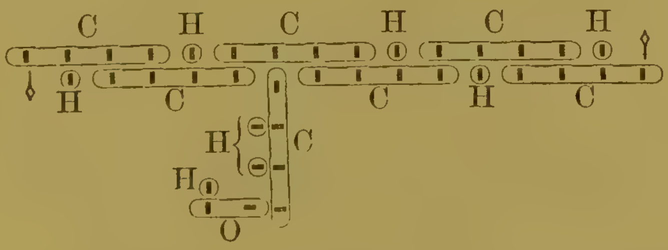
The constitution of phenol being thus understood, it is evident that this body could not have an isomer, neither has it; but its homologues have isomers which are true alcohols.

As toluene, xylene, etc., are only benzine one or more atoms of the hydrogen of which are replaced by alcohol radicles, so also its homologues are derived from phenol by the substitution of alcohol radicles for hydrogen; cresylic phenol, for example, is methylated phenol:



It will be seen from the above diagram that cresylic phenol is derived from toluene by the substitution of OH for H in the principal chain, and that this hydroxyl, being under the same conditions as in ordinary phenol, should possess the same properties.

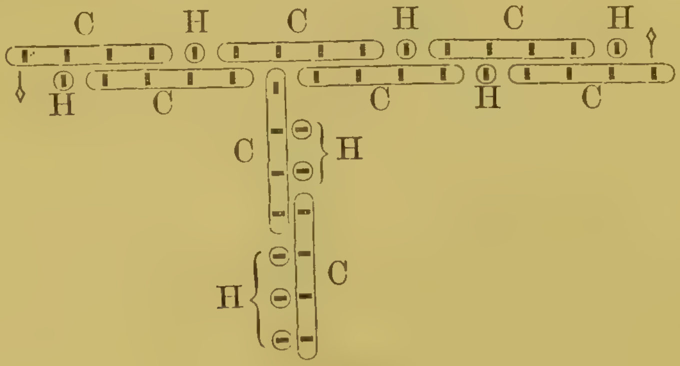
But if we suppose hydroxyl to be substituted for hydrogen in methyl, which in our diagram forms a lateral chain—



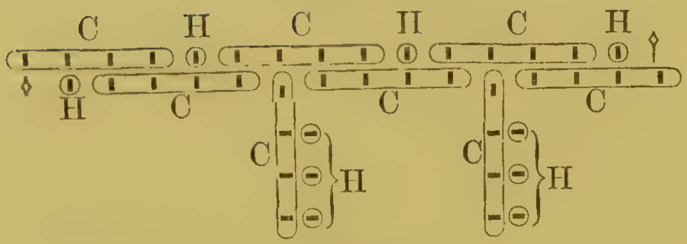
the same atom of carbon which holds this hydroxyl also holds $H^2$, which consequently may be exchanged for O and give rise to an acid. The compound which would have this constitution should therefore present characteristics analogous to those of alcohols proper, which it really does.

As we go higher in the aromatic series, we can conceive for one and the same term of this series several phenols and several alcohols, isomers, derived from several hydrocarbides also isomers.

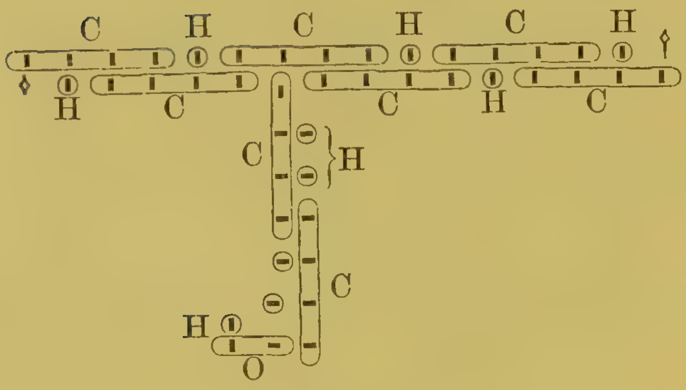
Thus we have seen that there exist two hydrocarbides having the formula $(C^8H^{16})$; each of these hydrocarbides may furnish an alcohol and a phenol:



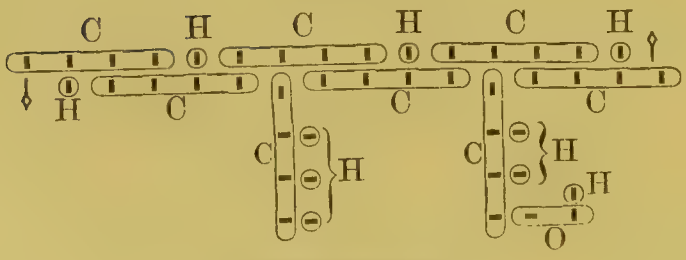
$= (C^8H^{10})\ \alpha$



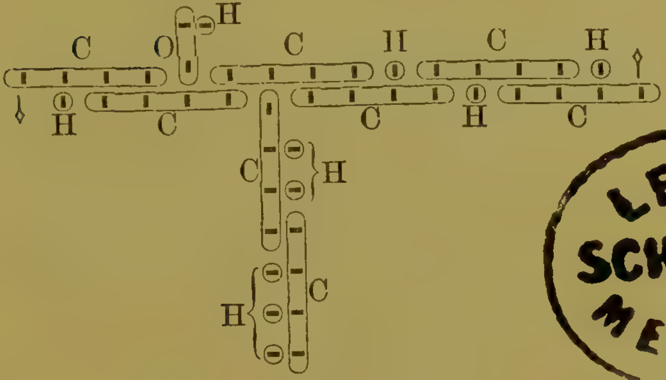
$= (C^8H^{10})\ \beta$



$=$ Alcohol $(C^8H^{10}O)\ \alpha$



$=$ Alcohol $(C^8H^{10}O)\ \beta$



= Phenol $(C^8H^{10}O)\alpha$

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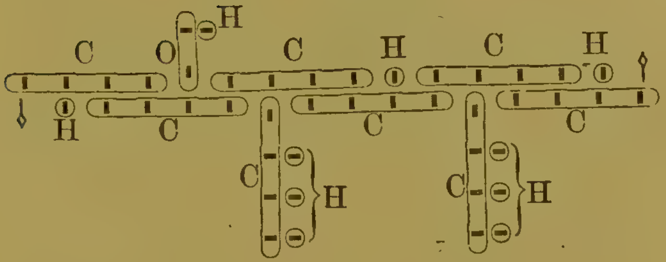
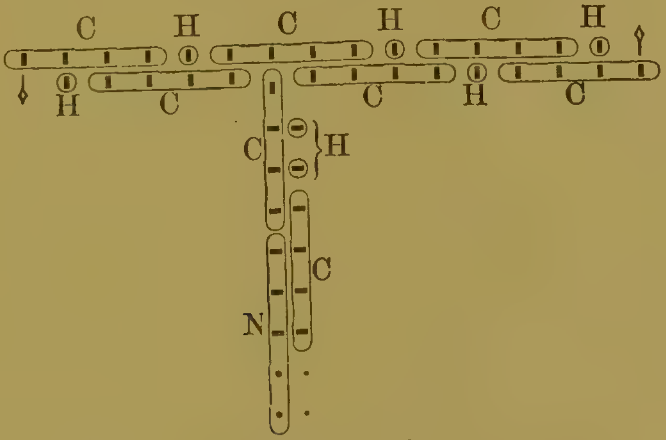


= Phenol $(C^8H^{10}O)\beta$

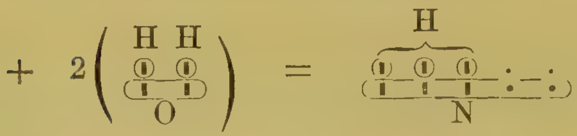
Therefore, to each hydrocarbide homologous with benzine there corresponds a phenol and an alcohol, and these two bodies differ in that the alcohol arises from the substitution of OH for H on a lateral chain, while in the phenol the substitution is on the principal chain itself.

When speaking of the preparation of monatomic acids, we have seen that the cyanides of aromatic alcohol radicles, on becoming hydrated, give acids isomeric with benzoic acid and its homologues; it is probable that the cyanides of the radicles of phenols would, on being hydrated, give true homologues of benzoic acid.

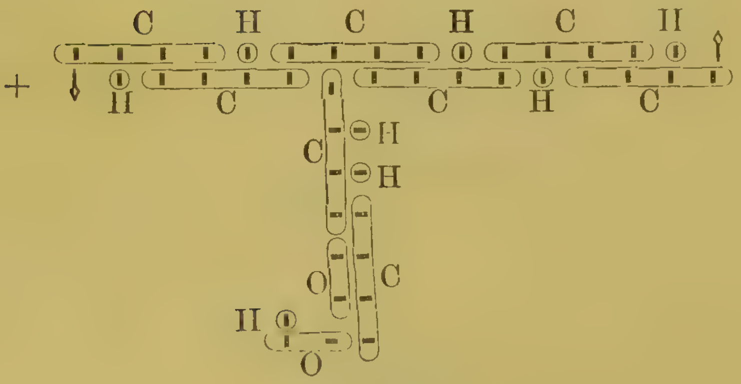
The following diagrams show that the hydration of cyanide of benzyl and cyanide of cresyl should produce two isomeric acids:



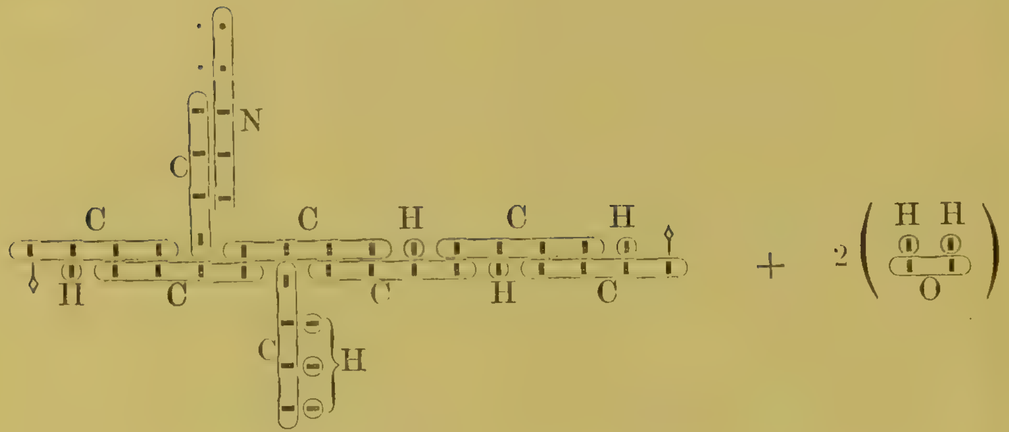
Cyanide of benzyl.



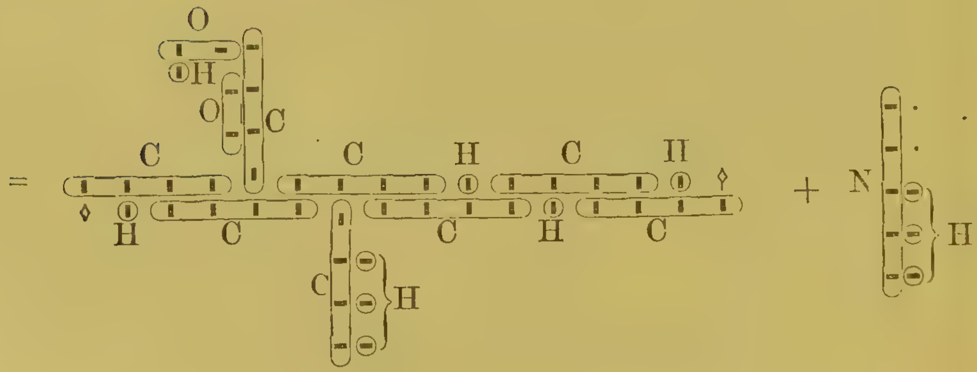
Water. Ammonia.



Alphatoluic acid.



Cyanide of cresyl. Water.



Toluic acid. Ammonia.

We said, when speaking of aromatic hydrocarbides, that the theory of M. Kékulé does not explain clearly the combination of benzine with $Cl^6$ or $Br^6$.

However this may be, this theory, the only one as yet which accounts for the numerous isomerisms observed in the aromatic series, is correctly based, and the deficiency mentioned cannot be regarded as a serious argument against it, as, after all, the grouping of benzine may easily be modified under the influence of chlorine or bromine.

**List of the Phenols actually known.**—1st. MONATOMIC PHENOLS.—Ordinary phenol, extracted from the oils of pit-coal ($C^6H^6O$).

Cresylic phenol, or cresylol, which is extracted from creosote ($C^7H^8O$).

Phloretic phenol, resulting from the splitting up of the acid of the same name ($C^9H^{12}O$).

Thymotic phenol, or thymol, which exists in the essence of thyme ($C^{10}H^{14}O$).

2nd. BIATOMIC PHENOLS. — Pyrocatechic phenol, or pyrocatechol ($C^6H^6O^2$), obtained by the dry distillation of catechu.

Guaiacic phenol, obtained by the distillation of the resin of guaiacum; and orcin, obtained by the decomposition of an erythride called erythrin. Both these phenols have the formula ($C^7H^8O^2$).

Veratrol ($C^8H^{10}O^2$), which is prepared by distilling an acid (veratric acid) contained in plants of the veratrum species.

3rd. TRIATOMIC PHENOLS.—Pyrogallic phenol, or pyrogallol, obtained by the dry distillation of gallic acid; franguline and phloro-glucine, all of which have for formula ($C^6H^6O^3$).

Alizaric phenol, or alizarin ($C^{10}H^6O^3$), the colouring principle of madder (*Rubia tinctorum*).

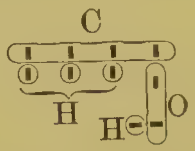
There should, perhaps, be added to this list hæmatin, the colouring principle of logwood, the formula of which ($C^{16}H^{14}O^6$) would be that of a hexatomic phenol; and œnoline, the colouring principle of wine, the composition of which ($C^{10}H^{10}O^5$) corresponds to that of a pentatomic phenol.

## GENERAL CONSIDERATIONS ON ATOMICITY AND BASICITY.

We have seen that the atomicity of a molecule consists in the number of atoms of typical hydrogen it contains, that is to say, of hydrogen that can be readily replaced by other radicles; while basicity expresses the number of atoms of hydrogen for which alkaline metals may be substituted by double decomposition with bases.

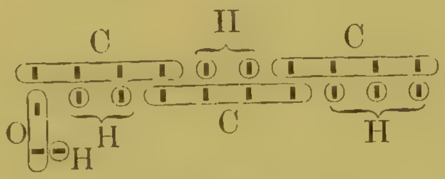
M. Kékulé has given the following explanation—which we think correct—of the causes to which the properties of typical and basic hydrogen are respectively owing:

In the carbides of hydrogen, all the hydrogen is united directly to the carbon, but it is possible for an atom of hydrogen to be eliminated and for an atom of oxygen to take its place. But as oxygen is biatomic it is not saturated on uniting with the carbon by only one of its atomicities, and therefore by the other it combines with an atom of hydrogen:



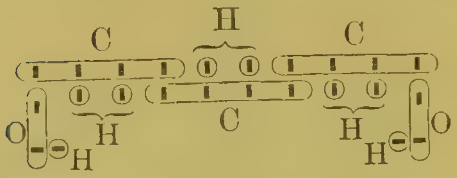
The above figure represents the oxygenized molecule thus formed. It will be seen that it contains three atoms of hydrogen united directly to the carbon, and a fourth which is united to it only by means of the oxygen. This last is typical hydrogen; the oxygen which serves as bond between it and the carbon has been called oxygen of addition, and, although this term is incorrect, we shall retain it for want of a better. It will be seen that, if the hypothesis of M. Kékulé be true, each atom of the oxygen of addition should render an atom of hydrogen typical, so that the atomicity of a molecule should always be equal to the number of atoms of oxygen of addition it contains.

The hydrogen rendered typical in the manner just indicated is alcoholic hydrogen, and the bodies of which it forms part are alcohols. The following figures represent the composition of propyl-alcohol and of propyl-glycol:



Propyl-alcohol.

$= C^3H^8O.$



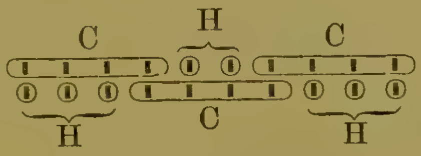
Propyl-glycol.

$= C^3H^8O^2.$

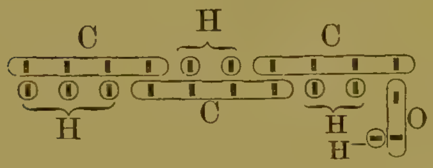
In order that the typical hydrogen may become basic, it is necessary that for its two adjoining atoms of hydrogen a second atom of oxygen be substituted. It will be conceived from this that if, in a polyatomic alcohol, the substitution only takes place in the neighbourhood of one atom of typical hydrogen, and not in that of others, that alone becomes basic where the substitution takes place. The result is, that in order to transform all the typical into basic hydrogen, it is necessary to introduce as many atoms of oxygen of substitution as there are atoms of oxygen of addition.

If a smaller quantity of oxygen of substitution were introduced into the molecule, the number of atoms of hydrogen made basic would always be equal to the number of atoms of oxygen substituted. This explains why a polyatomic alcohol can give origin to several acids, all of the same atomicity as itself, but of a basicity varying with the quantity of oxygen substituted.

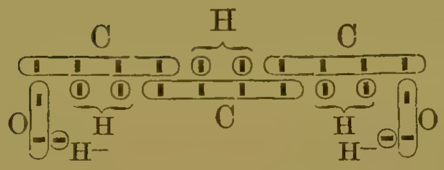
The following figures represent the constitution of hydride of propyl, propylic alcohol, propyl-glycol, propionic acid, lactic acid, and malonic acid. The basic hydrogen is marked by the sign +, and that which is typical by −:



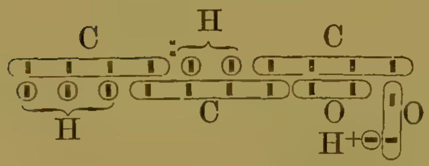
Hydride of propyl $C^3H^8$.



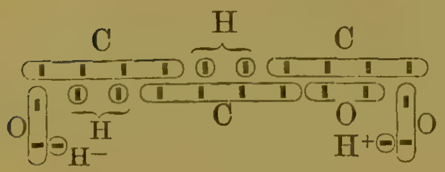
Propylic alcohol $C^3H^8O$.



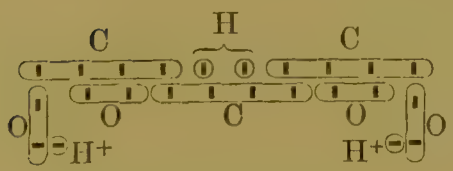
Propyl-glycol $C^3H^8O^2$



Propionic acid $C^3H^8O^2$.



Lactic acid $C^3H^6O^3$.



Malonic acid $C^3H^4O^4$.

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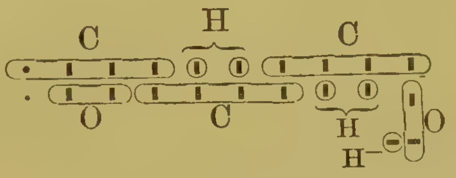
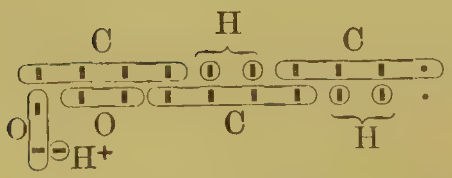
It will be seen that lactic acid should be monobasic though it is biatomic, while malonic acid is biatomic and bibasic. It will also be seen that, according as the group $OH^+$ or the group $OH^-$ is removed from lactic acid, neutral or acid monatomic residues will be formed:



$$= \left(C^3H^4O'' \left\{\begin{matrix}OH^- \\ \cdot\end{matrix}\right.\right)$$

Neutral monatomic residue of lactic acid.



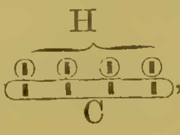
$$= \left(C^3H^4O'' \left\{\begin{matrix}\cdot \\ OH^+\end{matrix}\right.\right)$$

Acid monatomic residue of lactic acid.

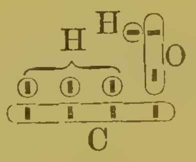
The hypothesis of M. Kékulé is verified in all the cases observed, with the exception of that of carbonic acid.

Carbonic acid does not exist, but bimetallic carbonates do; it is therefore certain that if this acid could be procured it would be bibasic. Besides, sulpho-carbonic acid $\left(\left.\begin{matrix}CS'' \\ H^2\end{matrix}\right\} S^2\right)$ is known, and it is bibasic, which comes to the same thing. Thus carbonic acid should be considered as the first term of the series to which lactic acid belongs; it appears, therefore, that it ought to be only monobasic, like its homologues, because, like them, it contains only a single atom of oxygen of substitution.

However, the anomaly of carbonic acid is easily explained, and does not affect the views of M. Kékulé. The hydride of methyl being

$CH^4$ = , methylic alcohol will be:

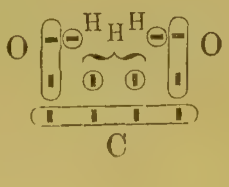
$$\left(C\left\{\begin{matrix}OH \\ H \\ H \\ H\end{matrix}\right.\right) =$$



$$= \left(\left.\begin{matrix}CH^3 \\ H\end{matrix}\right\} O\right)$$

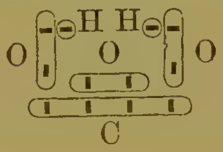
and methylenic glycol will be,

$$\left(C\left\{\begin{matrix}OH \\ H \\ H \\ OH\end{matrix}\right.\right) =$$

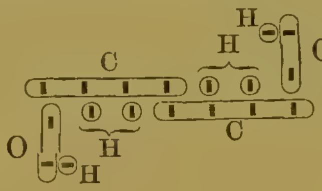


$$= \left(\left.\begin{matrix}CH^{2''} \\ H\end{matrix}\right\} O^2\right)$$

It is very evident that methyl-glycol containing only two atoms of non-typical hydrogen, cannot exchange $H^4$ for $O^2$, but only $H^2$ for O. If we represent this substitution by a diagram, we shall have the figure :



As is seen by these figures, the molecule of methyl-glycol only contains two atoms of non-typical hydrogen; the substitution of oxygen for these two atoms consequently furnishes a molecule of which the two atoms of typical hydrogen have each an atom of the oxygen of substitution near them, and are therefore basic. The same fact could not be produced with an alcohol, which would contain more than one atom of carbon, and consequently more than two atoms of non-typical hydrogen. In this case one of the groups OH would be separated from the oxygen of substitution, and would therefore contain typical, not basic hydrogen. The following figures render this explanation easy to be understood :



$= \left.\begin{matrix}C^2H^{4''}\\H^2\end{matrix}\right\}O^2$

Ordinary glycol.

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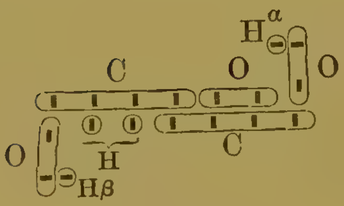


$= \left.\begin{matrix}C^2H^2O''\\H^2\end{matrix}\right\}O^2$

Glycolic acid.

The group OH, which contains the hydrogen marked $\alpha$, touches the atom of oxygen substituted, while the group OH, which contains the hydrogen $\beta$ is very distant from it.

## ALDEHYDS.

The name of aldehyds is given to bodies which are intermediate between the alcohols whence they are derived by elimination of hydrogen, and the acids from which they differ by containing less oxygen.

In order to understand the formation of the aldehyds, it should be remembered that alcohols possess the property of losing hydrogen, for which an equivalent quantity of oxygen may be substituted. This substitution takes place in two distinct stages: first, the alcohol is dehydrogenized, then it becomes oxidized. The intermediate product which is dehydrogenized and not yet oxidized is an aldehyd. It will be seen from this that the monatomic alcohols which can only exchange $H^2$ for O once, should give rise to a single aldehyd, while to biatomic alcohols, which can undergo this substitution twice, two aldehyds should correspond, and, generally, to alcohols of an atomicity equal to *n*, *n* aldehyds.

The aldehyds derived from monatomic alcohols are the best known.

## ALDEHYDS DERIVED FROM MONATOMIC ALCOHOLS.

These contain two atoms of hydrogen less than the alcohols, and an atom of oxygen less than the acids to which they correspond:

| | | |
|---|---|---|
| $(C^2H^6O)$<br>Alcohol. | $(C^2H^4O)$<br>Aldehyd. | $(C^2H^4O^2)$<br>Acetic acid. |
| $(C^7H^8O)$<br>Benzyl-alcohol. | $(C^7H^6O)$<br>Benzyl-aldehyd. | $(C^7H^6O^2)$<br>Benzoic acid. |

PREPARATION.—*First Process.*—Aldehyds are prepared by the oxidation of alcohols; hydrogen is separated in the state of water, and an aldehyd is formed:

$$\underset{\text{Amylic alcohol.}}{2(C^5H^{12}O)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} = \underset{\text{Valeric aldehyd.}}{2(C^5H^{10}O)} + \underset{\text{Water.}}{2(H^2O)}$$

*Second Process.*—Aldehyds may also be produced by causing chlorine to act on a diluted alcohol; but as the same result does not take place with absolute alcohols, and as moreover this formation of aldehyd by chlorine is always accompanied by that of a certain quantity of acid, it must be admitted that chlorine, in this case, acts simply as an oxidizing agent.

*Third Process.*—These bodies may be obtained by distilling an intimate mixture of formiate of calcium and a calcic salt of the acid corresponding to the aldehyd to be prepared:

$$\underset{\text{Benzoate of calcium.}}{[(C^7H^5O^2)^2Ca'']} + \underset{\text{Calcic formiate.}}{[(CHO^2)^2Ca'']} = \underset{\text{Calcic carbonate.}}{2\left(\left.\begin{matrix}CO''\\Ca''\end{matrix}\right\}O^2\right)} + \underset{\text{Benzoic aldehyd.}}{2(C^7H^6O)}$$

*Fourth Process.*—Hydride of copper is made to act on the chloride of an acid radicle:

$$\underset{\text{Chloride of benzoyl.}}{2\left(\left.\begin{matrix}C^7H^5O\\Cl\end{matrix}\right\}\right)} + \underset{\text{Hydride of copper.}}{(Cu^2H^2)} = \underset{\text{Protochloride of copper.}}{(Cu^2Cl^2)} + \underset{\text{Benzoic aldehyd.}}{2(C^7H^6O)}$$

This process, the discovery of which is due to M. Chiozza, gives very little aldehyd, as the greater part of the hydride of copper is decomposed without taking part in the reaction.

*Fifth Process.*—M. Lippemann has prepared benzoic aldehyd by acting upon the chloride of benzoyl by nascent hydrogen, developed by causing dry gaseous hydrochloric acid to act on sodium amalgam.

*Sixth Process.*—A cyanide of an acid radicle is prepared by causing the chloride of the same radicle to act on the cyanide of potassium, or what is better, on dry cyanide of silver. Nascent hydrogen, on reacting with this cyanide of an acid, furnishes hydrocyanic acid and an aldehyd:

$$\underset{\text{Chloride of benzoyl.}}{(C^7H^5OCl)} + \underset{\text{Cyanide of silver.}}{(AgCy)} = \underset{\text{Chloride of silver.}}{(AgCl)} + \underset{\text{Cyanide of benzoyl.}}{(C^7H^5OCy)}$$

$$\underset{\text{Cyanide of benzoyl.}}{2(C^7H^5OCy)} + \underset{\text{Hydrogen.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}\right)} = \underset{\text{Hydrocyanic acid.}}{2\left(\left.\begin{matrix}H\\Cy\end{matrix}\right\}\right)} + \underset{\text{Benzoic aldehyd.}}{2(C^7H^6O)}$$

*Seventh Process.*—Besides these processes which are general, certain aldehyds may be prepared by the division of certain natural principles. Thus amygdalin, a glucoside contained in bitter almonds, can give rise to benzoic aldehyd on being saponified by dilute acids, or by emulsin, a ferment contained in the same almonds:

$$\underset{\text{Amygdalin.}}{(C^{20}H^{27}NO^{11})} + \underset{\text{Water.}}{2(H^2O)} = \underset{\text{Benzoic aldehyd.}}{(C^7H^6O)} + \underset{\text{Hydrocyanic acid.}}{(CHN)} + \underset{\text{Glucose.}}{2(C^6H^{12}O^6)}$$

*Eighth Process.*—The essential oils contained in the seeds of certain plants sometimes contain aldehyds ready formed. Thus the oil of cumin contains cuminic aldehyd ($C^{10}H^{12}O$).

*Ninth Process.*—The dehydration of polyatomic alcohols may sometimes give rise to aldehyds which correspond to monatomic alcohols: at least one case of this kind is known. Ordinary glycerine, distilled with anhydrous phosphoric acid, gives rise to acrylic aldehyd (acrolein):

$$\underset{\text{Glycerine.}}{(C^3H^8O^3)} = \underset{\text{Water.}}{2(H^2O)} + \underset{\text{Acrylic aldehyd.}}{(C^3H^4O)}$$

PROPERTIES.—Aldehyds, to whatever series they belong, possess common properties. But there are also properties which distinguish the different series. We will first consider their common properties, then those which are distinctive.

*Properties common to all Aldehyds.*—1st. Under the slightest oxidizing influences, and sometimes even by simple exposure to the air, aldehyds can absorb an atom of oxygen and be transformed into monatomic acids:

$$\underset{\text{Valeric aldehyd.}}{2\,(C^5H^{10}O)} \quad + \quad \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} \quad = \quad \underset{\text{Valeric acid.}}{2\,(C^5H^{10}O^2)}$$

This property makes them powerful reducing agents.

2nd. Fused with potash the aldehyds are transformed into potassic salts of the corresponding monatomic acids, with disengagement of hydrogen:

$$\underset{\text{Cuminic aldehyd.}}{(C^{10}H^{12}O)} \quad + \quad \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} \quad = \quad \underset{\substack{\text{Cuminate of}\\\text{potassium.}}}{(C^{10}H^{11}KO^2)} \quad + \quad \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}}$$

3rd. Nascent hydrogen, obtained by the action of water on sodium amalgam, combines directly with aldehyds and transforms them into corresponding alcohols. If the aldehyd belong to a non-saturated series, the reaction is still the same, but nascent hydrogen is then fixed by the alcohol formed, and a saturated alcohol of another series is obtained:

$$\underset{\text{Acetic aldehyd.}}{(C^2H^4O)} \quad + \quad \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}} \quad = \quad \underset{\text{Ordinary alcohol.}}{(C^2H^6O)}$$

$$\underset{\text{Acrylic aldehyd.}}{(C^3H^4O)} \quad + \quad \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}} \quad = \quad \underset{\text{Allylic alcohol.}}{(C^3H^6O)} \quad + \quad \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}} \quad = \quad \underset{\text{Propylic alcohol.}}{(C^3H^8O)}$$

Nascent hydrogen, obtained by zinc and sulphuric acid, does not appear to unite with the aldehyds.

4th. When the pentachloride of phosphorus acts on an aldehyd, double decomposition takes place; oxychloride of phosphorus is formed, and a compound which represents the aldehyd employed the oxygen of which has been replaced by an equivalent quantity of chlorine:

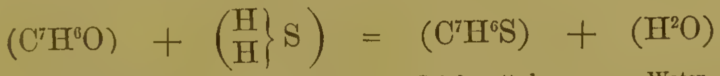
$$\underset{\text{Aldehyd.}}{(C^2H^4O)} \quad + \quad \underset{\substack{\text{Pentachloride of}\\\text{phosphorus.}}}{(PCl^5)} \quad = \quad \underset{\substack{\text{Oxychloride of}\\\text{phosphorus.}}}{(PCl^3O)} \quad + \quad \underset{\substack{\text{Chloride of ethy-}\\\text{lidene.}}}{(C^2H^4Cl^2)}$$

The chlorinated bodies thus produced have the same composition as the dichlorhydric ethers of glycols and as the monochlorinated hydrochloric ethers of the alcohols of the same series:

$$\underset{\substack{\text{Chloride of ethy-}\\\text{lidene.}}}{(C^2H^4Cl^2)} \qquad \underset{\substack{\text{Chloride of ethy-}\\\text{lene.}}}{(C^2H^4Cl^2)} \qquad \underset{\substack{\text{Chlorinated chloride}\\\text{of ethyl.}}}{(C^2H^4Cl.Cl)}$$

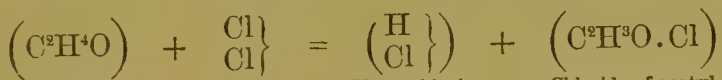
M. Beilstein had stated that the chlorides derived from aldehyds were identical with the chlorinated hydrochloric ethers of alcohols of the same series, basing this opinion on experiments he had made in the acetic and benzoic series. Later, however, Friedel showed that such identity did not exist in the valeric series; and still later I have demonstrated that—contrary to the views of M. Beilstein—it does not exist in the benzoic series. If, therefore, chlorinated chloride of ethyl and chloride of ethylidene are identical, which is doubtful, it is an isolated fact which does not appear in the other series. The bodies of the three classes above mentioned should be considered as isomers.

5th. Hydrosulphuric acid exchanges its sulphur for the oxygen of aldehyds, and sulphuretted aldehyds are produced. Sometimes these bodies remain combined with an excess of hydrosulphuric acid, but on submitting these compounds to the action of sulphuric or hydrochloric acid, the sulphuretted aldehyd is isolated from the sulphuretted hydrogen which is set free. This latter phenomenon is observed in the case of acetic aldehyd:

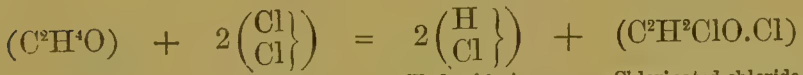


$$\underset{\text{Benzoic aldehyd.}}{(C^7H^6O)} + \underset{\text{Sulphuretted hydrogen.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}S\right)} = \underset{\text{Sulphuretted benzoic aldehyd.}}{(C^7H^6S)} + \underset{\text{Water.}}{(H^2O)}$$

6th. When chlorine or bromine acts on an aldehyd, phenomena of substitution arise. The monochlorinated or monobrominated product is identical with the chloride or bromide of the radicle of the acid corresponding to the aldehyd, and the ultimate products of substitution are the same as the products of substitution of these same chlorides or bromides:



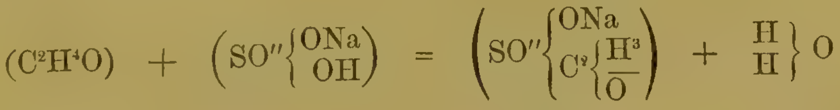
$$\underset{\text{Acetic aldehyd.}}{(C^2H^4O)} + \underset{\text{Chlorine.}}{\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}} = \underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Chloride of acetyl.}}{(C^2H^3O.Cl)}$$



$$\underset{\text{Acetic aldehyd.}}{(C^2H^4O)} + \underset{\text{Chlorine.}}{2\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}\right)} = \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Chlorinated chloride of acetyl.}}{(C^2H^2ClO.Cl)}$$

Wurtz has shown that the trichlorinated products of substitution of aldehyds are isomeric, and not identical, as has been hitherto admitted with the bodies obtained by the action of chlorine on absolute alcohols (chloral, chloramylal, etc.).

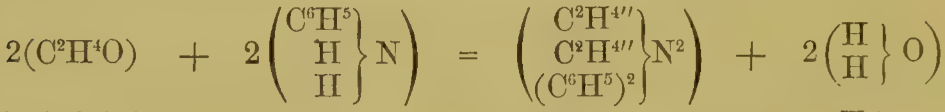
7th. All the aldehyds enter into double decomposition with the acid sulphites of the alkalies:



$$\underset{\text{Acetic aldehyd.}}{(C^2H^4O)} + \underset{\text{Acid sulphite of sodium.}}{\left(SO''\left\{\begin{matrix}ONa\\OH\end{matrix}\right.\right)} = \underset{\text{Bisulphite of acetyl-sodium.}}{\left(SO''\left\{\begin{matrix}ONa\\C^2\left\{\begin{matrix}H^3\\\overline{O}\end{matrix}\right.\end{matrix}\right.\right)} + \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O}$$

The compounds thus formed are crystallized, and dissolve in water. This reaction, discovered by Bertagnini, is utilized for the separation of aldehyds from bodies with which they are often mixed; and moreover it is so general that it may be used to find out whether a body is an aldehyd or not.

8th. Aniline combines with aldehyds, eliminating water and giving diamines isomeric with those derived from glycol :



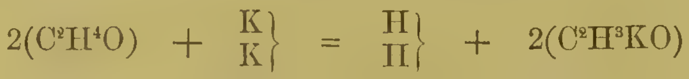
$$2(C^2H^4O) + 2\left(\left.\begin{matrix}C^6H^5\\ H\\ H\end{matrix}\right\}N\right) = \left(\left.\begin{matrix}C^2H^{4\prime\prime}\\ C^2H^{4\prime\prime}\\ (C^6H^5)^2\end{matrix}\right\}N^2\right) + 2\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)$$

Acetic aldehyd. Aniline. Diphenylic diethylidene-diamine. Water.

Diphenylic ethylidene-diamine is isomeric with diphenylic ethylene-diamine.

The reaction of aniline with the aldehyds is so general, according to M. Schiff, that it may be used quite as well as the action of the acid sulphite of sodium, to determine whether a body acts as an aldehyd or not.

9th. Alkaline metals dissolve in aldehyds, disengaging a quantity of hydrogen equivalent to that of the metal dissolved:



$$2(C^2H^4O) + \left.\begin{matrix}K\\ K\end{matrix}\right\} = \left.\begin{matrix}H\\ H\end{matrix}\right\} + 2(C^2H^3KO)$$

Aldehyd. Potassium. Hydrogen. Potassic-aldehyd (acetylide of potassium).

10th. The simultaneous action of water, hydrocyanic and hydrochloric acids, on an aldehyd, gives rise to the formation of a monobasic biatomic acid of a higher series, or to the formation of an amide of the same acid. In the series of the fatty acids it is amides which are formed, while in the aromatic series, acids arise :

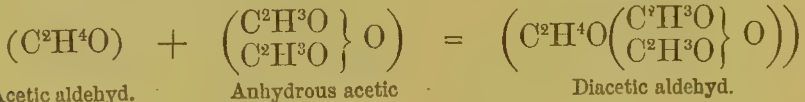
$$(C^2H^4O) + (CNH) + (H^2O) = (C^3H^7NO^2$$

Acetic aldehyd. Hydrocyanic acid. Water. Alanine (lactamidic acid.)

$$(C^7H^6O) + (CNH) + 2(H^2O) = (C^8H^7(NH^4)O^3)$$

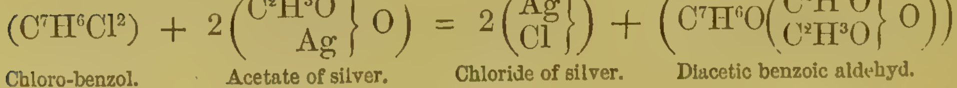
Benzoic aldehyd. Hydrocyanic acid. Water. Formobenzoate of ammonium.

11th. Aldehyds are capable of uniting directly with anhydrous acetic acid, and probably with other anhydrides of monobasic acids. Similar compounds are also obtained by submitting the chlorides derived from aldehyds by means of pentachloride of phosphorus, to the action of acetate of silver:



$$(C^2H^4O) + \left(\left.\begin{matrix}C^2H^3O\\ C^2H^3O\end{matrix}\right\}O\right) = \left(C^2H^4O\left(\left.\begin{matrix}C^2H^3O\\ C^2H^3O\end{matrix}\right\}O\right)\right)$$

Acetic aldehyd. Anhydrous acetic acid. Diacetic aldehyd.



$$(C^7H^6Cl^2) + 2\left(\left.\begin{matrix}C^2H^3O\\ Ag\end{matrix}\right\}O\right) = 2\left(\left.\begin{matrix}Ag\\ Cl\end{matrix}\right\}\right) + \left(C^7H^6O\left(\left.\begin{matrix}C^2H^3O\\ C^2H^3O\end{matrix}\right\}O\right)\right)$$

Chloro-benzol. Acetate of silver. Chloride of silver. Diacetic benzoic aldehyd.

These compounds are isomeric with the diacetic ethers of glycols;

they differ from them in that, under the influence of alkalies, they re-form an aldehyd instead of giving rise to a biatomic alcohol:

$$\underset{\text{Diacetic benzoic aldehyd.}}{\left(C^7H^6O\left(\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O\right)\right)} + \underset{\text{Potash.}}{2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic acetate.}}{2\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right)}$$

$$+ \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Benzoic aldehyd.}}{(C^7H^6O)}$$

$$\underset{\text{Diacetic glycol.}}{\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\(C^2H^3O)^2\end{matrix}\right\}O^2\right)} + \underset{\text{Potash.}}{2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic acetate.}}{2\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right)} + \underset{\text{Glycol.}}{\left(\left.\begin{matrix}C^2H^4\\H^{2\prime\prime}\end{matrix}\right\}O^2\right)}$$

*Properties peculiar to particular Series.*—Aldehyds are known which correspond to the fatty acids, and to the general formula $C^nH^{2n}O$; others which have the general formula $C^nH^{2n-2}O$, and which correspond to the acids $C^nH^{2n-2}O^2$. There are also some known which have the general formulæ $C^nH^{2n-8}O$ and $C^nH^{2n-10}O$; the first of these correspond to the aromatic acids $C^nH^{2n-8}O^2$, and the second to the acids $C^nH^{2n-10}O^2$.

The properties of the aldehyds of the first two series are similar, as are also those of the aldehyds of the last two series.

*Properties of the Aldehyds corresponding to the Formulæ* $C^nH^{2n}O$ and $C^nH^{2n-2}O$.—1st. When submitted to the influence of an alcoholic solution of potash, these bodies become resinous.

2nd. They combine directly with ammonia, producing crystallized compounds. These represent the aldehyd employed, one atom of hydrogen of which is replaced by ammonium:

$$\underset{\text{Acetic aldehyd.}}{(C^2H^4O)} + \underset{\text{Ammonia.}}{(NH^3)} = \underset{\substack{\text{Aldehydate of ammonia}\\\text{(acetylide of ammonium).}}}{C^2H^3(NH^4)O}$$

Treated with acids, these compounds give an ammoniacal salt and the aldehyd.

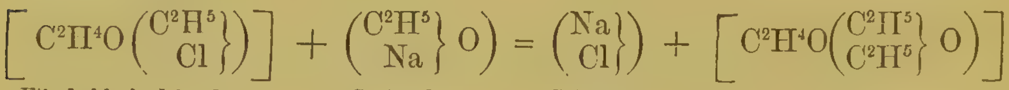
3rd. Nitric acid oxidizes them, but does not give products of nitrous substitution.

4th. When they are dissolved in absolute alcohol, and a current of hydrochloric acid is transmitted through the mixture, this becomes heated, and a compound is produced which represents a direct combination of the aldehyd with chloride of ethyl:

$$\underset{\text{Acetic aldehyd.}}{(C^2H^4O)} + \underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}} = \underset{\substack{\text{Ethyl-chlorhydrin of the}\\\text{aldehyd.}}}{\left(C^2H^4O\left(\left.\begin{matrix}C^2H^5\\Cl\end{matrix}\right\}\right)\right)}$$

$$+ \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

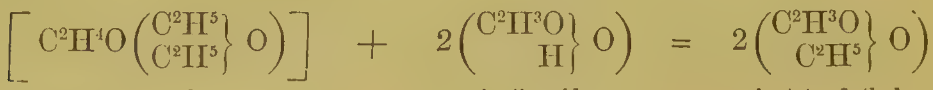
These ethyl-chlorhydrins react with the ethylate of sodium, and the group ($C^2H^5O$) is substituted for their chlorine. Products result which may be regarded as combinations of an aldehyd with oxide of ethyl. In the series of ordinary aldehyd, this combination has received the name of acetal:



$$\left[C^2H^4O\left(\left.\begin{matrix}C^2H^5\\ Cl\end{matrix}\right\}\right)\right] + \left(\left.\begin{matrix}C^2H^5\\ Na\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}Na\\ Cl\end{matrix}\right\}\right) + \left[C^2H^4O\left(\left.\begin{matrix}C^2H^5\\ C^2H^5\end{matrix}\right\}O\right)\right]$$

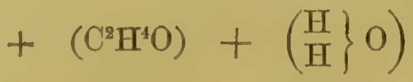
Ethyl-chlorhydrin of the aldehyd. Sodic ethylate. Chloride of sodium. Acetal.

Bodies analogous to acetal, when heated with acetic acid, furnish acetate of ethyl, and the aldehyd they contain becomes free:



$$\left[C^2H^4O\left(\left.\begin{matrix}C^2H^5\\ C^2H^5\end{matrix}\right\}O\right)\right] + 2\left(\left.\begin{matrix}C^2H^3O\\ H\end{matrix}\right\}O\right) = 2\left(\left.\begin{matrix}C^2H^3O\\ C^2H^5\end{matrix}\right\}O\right)$$

Acetal. Acetic acid. Acetate of ethyl.



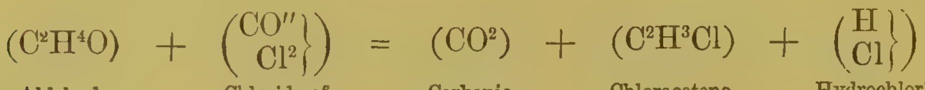
$$+ (C^2H^4O) + \left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)$$

Aldehyd. Water.*

5th. Acetal and analogous bodies are formed, but with difficulty, by the action of ethylate of sodium on chloride of ethylidene, or on bodies of the same nature.

6th. When left alone, the aldehyds of this group have a great tendency to become transformed into polymeric products.

7th. Oxychloride of carbon transforms ordinary aldehyd into a non-oxygenized chloride, which is used, as has been already seen, in the synthesis of cinnamic acid. It is probable that the other aldehyds of the same group would give analogous products under the influence of the same reagent:



$$(C^2H^4O) + \left(\left.\begin{matrix}CO''\\ Cl^2\end{matrix}\right\}\right) = (CO^2) + (C^2H^3Cl) + \left(\left.\begin{matrix}H\\ Cl\end{matrix}\right\}\right)$$

Aldehyd. Chloride of carbonyl. Carbonic anhydride. Chloracetene. Hydrochloric acid.

8th. When an aldehyd of the series $C^nH^{2n-2}O$ is strongly oxidized, besides the corresponding acid $C^nH^{2n-2}O^2$, there is always produced a small quantity of a more saturated acid belonging to the series $C^nH^{2n}O^2$. Thus, when acrolein ($C^3H^4O$) (acrylic aldehyd) is oxidized, there is formed, not only acrylic acid ($C^3H^4O^2$), but also acetic acid ($C^2H^4O^2$).

9th. When heated with slaked lime, these aldehyds give the calcic salt of the corresponding acid, along with the alcohol whence they are derived. In this case there are also formed secondary products, which have not been well studied:

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* This last reaction has not been proved by experiment. We have admitted it from analogy with what takes place in the other series.

$$\underset{\text{Valeral.}}{4\,(C^5H^{10}O)} + \underset{\text{Hydrate of calcium.}}{\left(\left.\begin{matrix}Ca''\\H^2\end{matrix}\right\}O^2\right)} = \underset{\text{Valerate of calcium.}}{\left[\left.\begin{matrix}(C^5H^9O)^2\\Ca''\end{matrix}\right\}O^2\right]} + \underset{\text{Amylic alcohol.}}{2\,(C^5H^{12}O)}$$

*Properties of the aldehyds having the general formulæ* $C^nH^{2n-8}O$ and $C^nH^{2n-10}O$.—1st. An alcoholic solution of potash does not cause these aldehyds to become resinous, and acts on them as slaked lime acts on those of the preceding group, but with greater clearness :

$$\underset{\text{Benzoic aldehyd.}}{2\,(C^7H^6O)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic benzoate.}}{\left(\left.\begin{matrix}C^7H^5O\\K\end{matrix}\right\}O\right)} + \underset{\text{Benzoic alcohol.}}{(C^7H^8O)}$$

2nd. Ammonia, instead of combining directly with these bodies, causes the elimination of water. The reaction takes place between three molecules of aldehyd and two of ammonia. The product formed is called hydramide :

$$\underset{\text{Benzoic aldehyd.}}{3\,(C^7H^6O)} + \underset{\text{Ammonia.}}{2\left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right)} = \underset{\text{Hydro-benzamide.}}{\left(\left.\begin{matrix}C^7H^{6''}\\C^7H^{6''}\\C^7H^{6''}\end{matrix}\right\}N^2\right)} + \underset{\text{Water.}}{3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

These hydramides, when boiled with dilute acids, become hydrated, and furnish an ammoniacal salt, while the aldehyd is re-formed. But if they be heated with an alkaline solution, they are transformed into an isomeric alkaloid which no longer reproduces the aldehyd in becoming hydrated.

3rd. With these aldehyds monohydrated nitric acid gives products of nitrous substitution :

$$\underset{\text{Benzoic aldehyd.}}{(C^7H^6O)} + \underset{\text{Nitric acid.}}{\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Mononitrated benzoic aldehyd.}}{(C^7H^5(NO^2)O)}$$

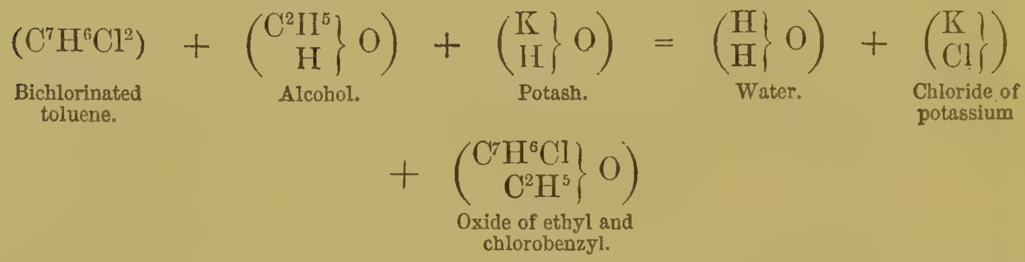
4th. When left to themselves these aldehyds do not become condensed; but it has been observed that benzoic aldehyd, mixed with hydrocyanic acid, is transformed, under the influence of alcoholic solution of potash, into a crystallized product, benzoin, which is benzoic aldehyd doubled :

$$\underset{\text{Benzoic aldehyd.}}{2\,(C^7H^6O)} = \underset{\text{Benzoin.}}{(C^{14}H^{12}O^2)}$$

Benzoin heated to redness returns to the state of benzoic aldehyd; if it be submitted to oxidizing influences, it gives benzilic acid ($C^{14}H^{12}O^3$).

Probably similar reactions might be obtained with the other aldehyds of the same group.

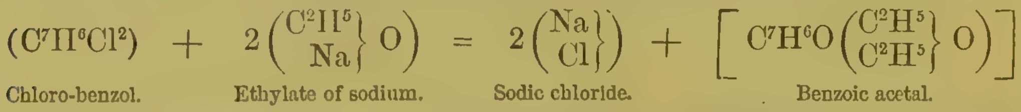
5th. I have ascertained that the simultaneous action of hydrochloric acid and absolute alcohol on benzoic aldehyd does not cause the formation of an ethyl-chlorhydrin. It is true that by treating bichlorinated toluene with alcoholic solution of potash, a compound is obtained which possesses the composition of benzoic ethyl-chlorhydrin :



$$\underset{\text{Bichlorinated toluene.}}{(C^7H^6Cl^2)} + \underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Chloride of potassium}}{\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)} + \underset{\text{Oxide of ethyl and chlorobenzyl.}}{\left(\left.\begin{matrix}C^7H^6Cl\\C^2H^5\end{matrix}\right\}O\right)}$$

But this body represents the mixed monochlorinated ethyl-benzilic oxide, and is not analogous to the ethyl-chlorhydrin obtained with acetic aldehyd ; in fact, it is not transformed by the ethylate of sodium into a product analogous to acetal; the chlorine it contains is in the principal chain.

6th. However, a body analogous to acetal is obtained in the benzoic series by submitting chloro-benzol to the action of ethylate of sodium :



$$\underset{\text{Chloro-benzol.}}{(C^7H^6Cl^2)} + \underset{\text{Ethylate of sodium.}}{2\left(\left.\begin{matrix}C^2H^5\\Na\end{matrix}\right\}O\right)} = \underset{\text{Sodic chloride.}}{2\left(\left.\begin{matrix}Na\\Cl\end{matrix}\right\}\right)} + \underset{\text{Benzoic acetal.}}{\left[C^7H^6O\left(\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}O\right)\right]}$$

7th. This acetal is transformed into benzoic aldehyd and acetate of ethyl, when heated to 100° with crystallizable acetic acid, as is shown by M. Cannizzaro's experiments.

8th. Aldehyds of the series $C^nH^{2n-10}O$ give, on being oxidized, not only the corresponding acid $C^nH^{2n-10}O^2$, but also a certain quantity of an acid of the series $C^nH^{2n-8}O^2$. Thus cinnamic aldehyd ($C^9H^8O$) gives not only cinnamic acid ($C^9H^8O^2$), but also benzoic acid ($C^7H^6O^2$).

9th. It is not known whether oxychloride of carbon reacts on the aldehyds of this group.

## RATIONAL FORMULÆ AND CONSTITUTION OF THE ALDEHYDS.

Aldehyds appear to have the same constitution as the acids which correspond to them, with the slight difference that the hydroxyl of these latter is replaced in the aldehyds by hydrogen. Thus (ROH) being a monatomic acid, (RH) would be the corresponding aldehyd.

By taking this view of the constitution of aldehyds, we are able to assign them formulæ which account for their principal reactions, and explain in what they are distinguished from their numerous isomers.

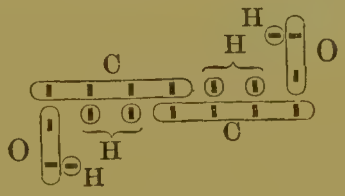
Without speaking of the isomerism of the aldehyds with acetone, which will be mentioned presently, every aldehyd is isomeric: 1st, with the anhydride of the glycol of the same series; 2nd, with the alcohol, either saturated or not, isologous with that whence the aldehyd is derived.

In order that this may be clearly understood, let us take acetic aldehyd ($C^2H^4O$) as example. This body is isomeric with oxide of ethylene and with acetylic alchol:

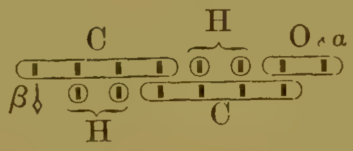
| $(C^2H^4O)$ | $(C^2H^4O)$ | $(C^2H^4O)$ |
|---|---|---|
| Aldehyd. | Oxide of ethylene. | Acetylic alcohol. |

How can the difference which exists between these three bodies be accounted for, considering their composition?

Let us first consider the anhydride of glycol. This body is evidently derived from glycol



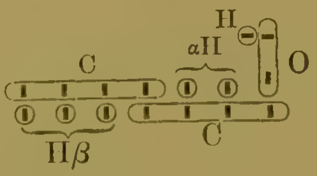
by elimination of $H^2O$. Moreover, if we consider that oxide of ethylene does not contain any typical hydrogen, while glycol contains two atoms, we shall be led to admit that the water eliminated contains these two atoms of typical hydrogen of the glycol, combined with one of its two atoms of oxygen, and the molecule thus truncated must necessarily take the form:



It will be seen that in such a molecule, there would remain two affinities unsaturated, one at a and the other at β. Now, as all incomplete molecules have always a great tendency to become saturated, it is very probable that these free affinities reciprocally saturate each other, and that according to M. Kékulé's happy expression, the chain closes: this is what is indicated by the marks placed at a and β.

Aldehyd, instead of being derived from glycol by dehydration, is derived from alcohol by dehydrogenation, or from acetic acid by deoxidation.

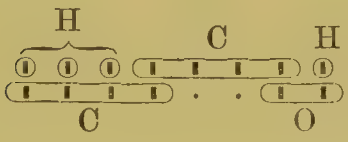
The molecule of alcohol being:



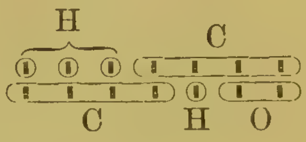
how can the aldehyd be formed?

*A priori*, two hypotheses are possible: either without changing the system, the alcohol loses $H^2$ at $\alpha$ or $\beta$; or two atoms of hydrogen being removed, the oxygen which was at first only united to the carbon by one of its atomicities, combines with it by both, and the last free atomicity of the carbon is saturated by hydrogen which was previously typical.

The following figures explain the constitution of aldehyd according to each of these hypotheses:



First hypothesis.



Second hypothesis.

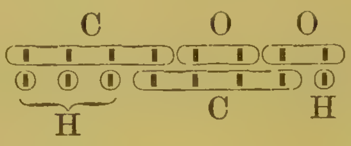
In the first, one atom of hydrogen would be united by means of the oxygen, and the molecule would not be saturated; in the second, all the atoms of hydrogen would be united directly to the carbon, and the molecule would be saturated.

If, therefore, the first hypothesis were true, the action of pentachloride of phosphorus should detach an atom of hydrogen from the aldehyd; if, on the contrary, the second hypothesis were correct, this reagent should simply cause the substitution of $Cl^2$ for O, without any division in the molecule being produced.

Experience having shown that the second alternative is what occurs, the first hypothesis must be rejected, and the second alone remains probable.

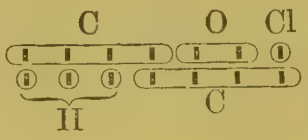
The same result is also arrived at when we examine in what way the aldehyds are derived from their respective acids.

For instance, let it be acetic acid:



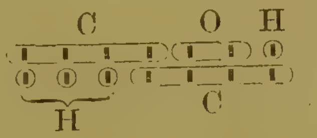
$$= C^2H^3O.OH$$

If this body be treated by pentachloride of phosphorus, the hydroxyl is detached and chlorine substituted; thus chloride of acetyl is obtained:



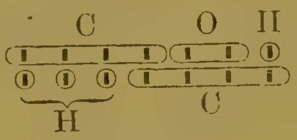
$$= C^2H^3OCl$$

Thus the chloride of acetyl when treated by nascent hydrogen exchanges its chlorine for hydrogen and furnishes aldehyd,* the molecule of which should consequently have the following form :

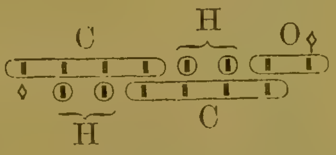


Guided by considerations of the atomic volumes—a subject which will be treated at the end of this work—M. Kopp considers that the oxygen of aldehyd is oxygen of substitution, that is to say, the oxygen united to the carbon by its two centres of attraction. This supports our manner of regarding aldehyd.

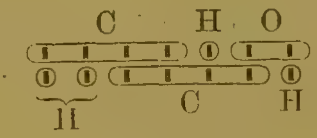
According to these views, the written formula of aldehyd would be $\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\\bar{O}\\H\end{matrix}\right.$. This formula clearly distinguishes it from its two isomers ; it shows that in aldehyd the oxygen is united to a single atom of carbon, while in oxide of ethylene, it must be admitted, as has just been seen, that it is united to two atoms of this metalloid ; and it also shows that aldehyd does not contain hydroxyl, while acetylic alcohol, in virtue of its being an alcohol, must necessarily contain one molecule. The molecules of aldehyd, oxide of ethylene and acetylic alcohol would, according to this, be composed in the manner represented in the following diagrams :



Aldehyd.



Oxide of ethylene.



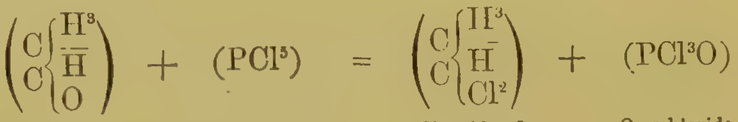
Acetylic alcohol.

Lieben, who first proposed the formulæ we have adopted to explain the isomerism of aldehyd and oxide of ethylene, has reviewed the different reactions of aldehyd, and has shown that they may be readily understood with the formula $\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\\bar{H}\\O\end{matrix}\right.$ : his work being of great importance, we will adopt his view.

---

* The experiment has not been tried in the acetic series, but it has succeeded in the benzoic, in which M. Lippemann has by this means transformed the chloride of benzoyl into oil of bitter almonds.

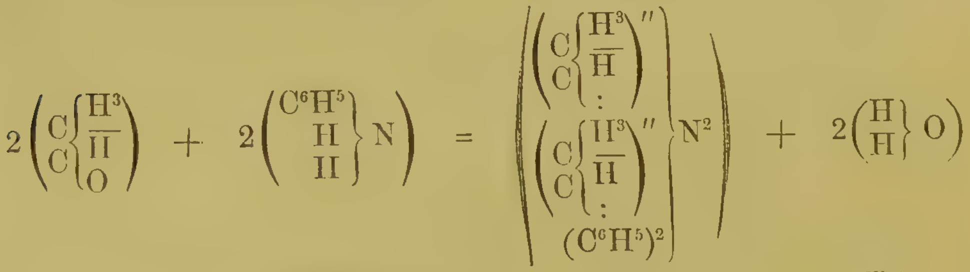
This formula accounts for—1st, the reaction of the pentachloride of phosphorus on aldehyd:



$$\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H^3\\ \hline H\\ O\end{array}\right.\right) + (PCl^5) = \left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H^3\\ \hline H\\ Cl^2\end{array}\right.\right) + (PCl^3O)$$

Aldehyd. Pentachloride of phosphorus. Chloride of ethylidene. Oxychloride of phosphorus.

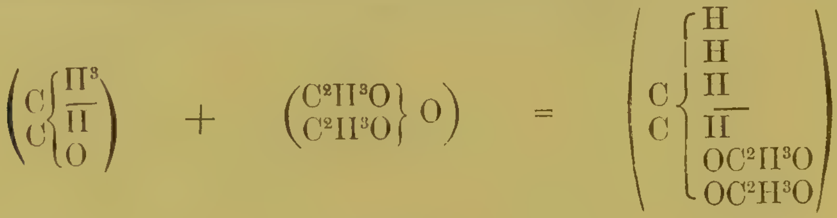
2nd. For the action exercised by aldehyd on phenylamine, in which action the radicle ethylidene ($C^2H^{4''}$) is substituted for $H^2$:



$$2\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H^3\\ \hline H\\ O\end{array}\right.\right) + 2\left(\left.\begin{matrix}C^6H^5\\ H\\ H\end{matrix}\right\}N\right) = \left(\left.\begin{matrix}\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H^3\\ \hline H\\ :\end{array}\right.\right)''\\ \left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H^3\\ \hline H\\ :\end{array}\right.\right)''\\ (C^6H^5)^2\end{matrix}\right|N^2\right) + 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

Aldehyd. Phenylamine. Diphenylic diethylidene diamine. Water.

3rd. For the direct combination of aldehyd with anhydrous acids and for its indirect combination with ethers proper:

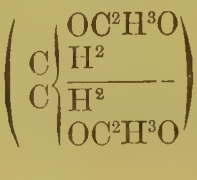


$$\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H^3\\ \hline H\\ O\end{array}\right.\right) + \left(\left.\begin{matrix}C^2H^3O\\ C^2H^3O\end{matrix}\right\}O\right) = \left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H\\ H\\ H\\ \hline H\\ OC^2H^3O\\ OC^2H^3O\end{array}\right.\right)$$

Aldehyd. Acetic anhydride. Acetal.

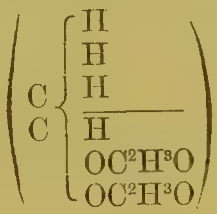
In this reaction, the atom of oxygen which saturated two centres of attraction of the carbon leaves one which unites with the typical oxygen of the acetic anhydride, and each of the two atoms of oxygen again unites with a molecule of acetyl by its centre of attraction left free. The isomerism of acetal and diacetic glycol is thus easily explained, as, in this latter body, the two atoms of oxacetyl are united to two different atoms of carbon, while in acetal they are united to one and the same atom of this metalloid, as the following formulæ show:

EEDS
HOOL OF
DICINE



$$\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}OC^2H^3O\\ H^2\\ \hline H^2\\ OC^2H^3O\end{array}\right.\right)$$

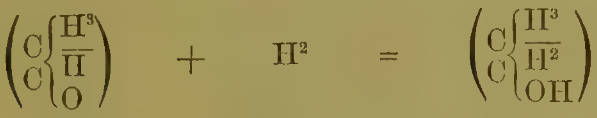
Diacetic glycol.



$$\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H\\ H\\ H\\ \hline H\\ OC^2H^3O\\ OC^2H^3O\end{array}\right.\right)$$

Acetal.

4th. For the transformation of aldehyd into alcohol, by means of nascent hydrogen:

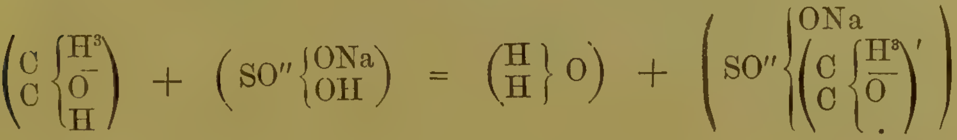


$$\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H^3\\\hline H\\O\end{array}\right.\right) + H^2 = \left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H^3\\\hline H^2\\OH\end{array}\right.\right)$$

Aldehyd. Hydrogen. Alcohol.

Here, as in the preceding case, the atom of oxygen leaves one of the centres of attraction of the carbon; there results a free affinity of carbon and a free affinity of oxygen; these are saturated by two atoms of hydrogen.

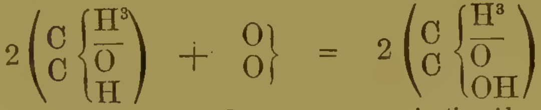
5th. For the reaction of aldehyd with acid sulphites of the alkalies:



$$\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H^3\\\hline O\\H\end{array}\right.\right) + \left(SO''\left\{\begin{matrix}ONa\\OH\end{matrix}\right.\right) = \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + \left(SO''\left\{\begin{array}{l}ONa\\\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H^3\\\hline O\\ .\end{array}\right.\right)'\end{array}\right.\right)$$

Aldehyd. Acid sulphite of sodium. Water. Acid sulphite of acetyl-sodium.

6th. For the transformation of aldehyd into acetic acid by direct oxidation:

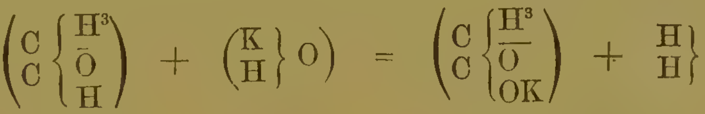


$$2\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H^3\\\hline O\\H\end{array}\right.\right) + \left.\begin{matrix}O\\O\end{matrix}\right\} = 2\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H^3\\\hline O\\OH\end{array}\right.\right)$$

Aldehyd. Oxygen. Acetic acid.

The reaction consists in the substitution of the halogen residue of water (OH) for hydrogen (H).

7th. For the transformation of aldehyd into acetate of potassium, with disengagement of hydrogen, when fused with potash:

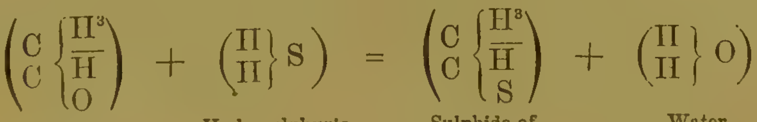


$$\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H^3\\\hline O\\H\end{array}\right.\right) + \left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right) = \left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H^3\\\hline O\\OK\end{array}\right.\right) + \left.\begin{matrix}H\\H\end{matrix}\right\}$$

Aldehyd. Potash. Potassic acetate. Hydrogen.

This reaction is only a double decomposition in which the residue OK of the potassic hydrate is substituted for the hydrogen of the aldehyd.

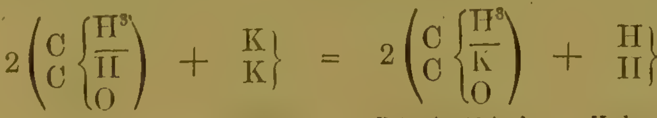
8th. For the action exercised by hydrosulphuric acid on aldehyd:



$$\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H^3\\\hline H\\O\end{array}\right.\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}S\right) = \left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H^3\\\hline H\\S\end{array}\right.\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

Aldehyd. Hydrosulphuric acid. Sulphide of ethylidene. Water.

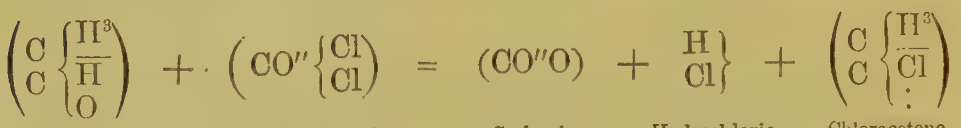
9th. For the substitution of alkaline metals for the hydrogen of aldehyd:



$$2\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H^3\\\hline H\\O\end{array}\right.\right) + \left.\begin{matrix}K\\K\end{matrix}\right\} = 2\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}H^3\\\hline K\\O\end{array}\right.\right) + \left.\begin{matrix}H\\H\end{matrix}\right\}$$

Aldehyd. Potassium. Potassic aldehyd. Hydrogen.

10th. For the reaction of oxychloride of carbon on aldehyd:

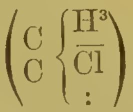


$$\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\\overline{H}\\O\end{matrix}\right.\right)+\left(CO''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)=(CO''O)+\left.\begin{matrix}H\\Cl\end{matrix}\right\}+\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\\overline{Cl}\\:\end{matrix}\right.\right)$$

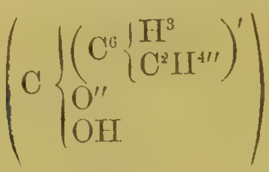
Aldehyd. Oxychloride of carbon. Carbonic anhydride. Hydrochloric acid. Chloracetene.

The chloracetene produced is a non-saturated body; its form is the same as that free ethylidene would have, if it existed. M. Lieben, considering that ethylidene represents methylene $CH^2$, of which H is replaced by $CH^3$, deduced from this resemblance an additional proof in favour of the formula he adopted for aldehyd: he attributed the non-existence of free ethylidene to the same unknown cause which prevents methylene from existing. This reasoning is fallacious, because chloracetene exists, and has the same constitution as ethylidene; unless, indeed, chlorine is trivalent in chloracetene.

However it may be with the argument taken by M. Lieben from the non-existence of ethylidene, nothing conclusive has been advanced against the formula proposed by him for aldehyd, which, as we have just seen, admirably accounts for everything we know concerning this body.

Moreover, the formula of chloracetene itself  $\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\\overline{Cl}\\:\end{matrix}\right.\right)$ is founded on the action exercised by this body on potassic benzoate, in which cinnamic acid is formed.

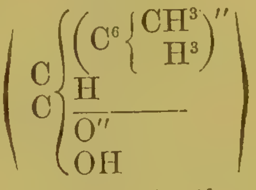
The analogies of cinnamic with acrylic acid, the constitution of which Mr. Frankland has recently established with so much clearness, prove that the first of these acids corresponds to the formula:



$$\left(C\left\{\begin{matrix}\left(C^6\left\{\begin{matrix}H^3\\C^2H^{4''}\end{matrix}\right.\right)'\\O''\\OH\end{matrix}\right.\right)$$

Ethylene-benzoic acid.

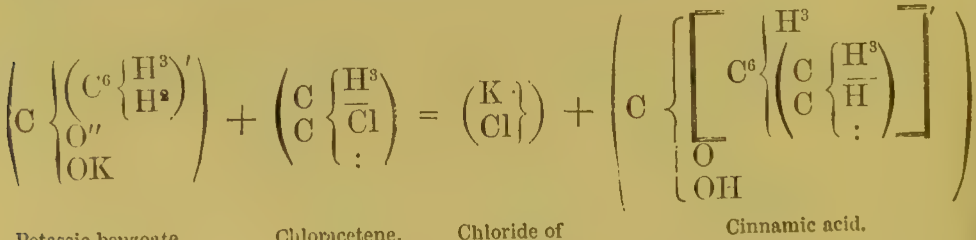
or to the formula



$$\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}\left(\left(C^6\left\{\begin{matrix}CH^3\\H^3\end{matrix}\right.\right)''\right.\\\underline{H}\\O''\\OH\end{matrix}\right.\right)$$

Toluene-acetic acid.

Now, with the first of these formulæ the synthetical production of cinnamic acid is well explained, on condition that the formula we propose for chloracetene be also admitted. We have:



$$\left(C\left\{\begin{matrix}\left(C^6\left\{\begin{matrix}H^3\\H^2\end{matrix}\right.\right)'\\O''\\OK\end{matrix}\right.\right)+\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\\overline{Cl}\\:\end{matrix}\right.\right)=\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)+\left(C\left\{\begin{matrix}\left[C^6\left\{\begin{matrix}H^3\\\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\\overline{H}\\:\end{matrix}\right.\right)\end{matrix}\right.\right]'\\O\\OH\end{matrix}\right.\right)$$

Potassic benzoate. Chloracetene. Chloride of potassium. Cinnamic acid.

**Enumeration of the known Aldehyds of this group.**—We know:

1st. *In the series of fatty acids:*

| | |
|---|---|
| Acetic aldehyd | $C^2H^4O$ |
| Propionic aldehyd | $C^3H^6O$ |
| Butyric aldehyd | $C^4H^8O$ |
| Valeric aldehyd, or valeral | $C^5H^{10}O$ |
| Caproic aldehyd | $C^6H^{12}O$ |
| Œnanthylic aldehyd, or œnanthol | $C^7H^{14}O$ |
| Caprylic aldehyd | $C^8H^{16}O$ |

which all correspond to the general formula $C^nH^{2n}O$.

Formic aldehyd $CH^2O$ does not exist, and as oil of rue $C^{10}H^{20}O$ does not enter into double decomposition with aniline, it may be questioned whether it is an aldehyd.

2nd. *In the series of allylic alcohol and its homologues:*

Only acrylic aldehyd, or acrolein $C^3H^4O$.

As to the compound $C^5H^8O$, whose existence Gerhardt thinks probable in the oil of Roman camomile, and which he regards as angelic aldehyd, if it does exist it is not an aldehyd, as it does not combine with acid sulphites of the alkalies.

3rd. *In the series of benzoic acid and its homologues:*

| | |
|---|---|
| Benzoic aldehyd, or oil of bitter almonds | $C^7H^6O$ |
| Toluic aldehyd | $C^8H^8O$ |
| . . . . . . . . . . . . . . . . . . . . . | |
| Cuminic aldehyd (the oxygenized part of oil of cumin) | $C^{10}H^{12}O$ |
| Sycocerylic aldehyd | $C^{18}H^{28}O$ |

which all correspond to the general formula $C^nH^{2n-8}O$.

4th. *In the series of cinnamic acid:*

Cinnamic aldehyd, or oxygenized oil of cinnamon $C^9H^8O$.

The aldehyds of the series intermediate between that to which acrolein belongs and those in which the aromatic aldehyds are classed are not known. Laurel camphor $C^{10}H^{16}O$, it is true, has been considered as the aldehyd of campholic alcohol $C^{10}H^{18}O$, but its properties remove it from the aldehyds: instead of disengaging hydrogen under the influence of potash at a red heat, and giving a salt of the corresponding acid, camphor unites directly with this alkali, producing a salt, the potassic campholate, which does not belong to the same series as its generator. Moreover, camphor does not unite either with acid sulphites of the alkalies or with aniline. Finally, under the influence of oxidizing agents, camphor absorbs not one, but three atoms of oxygen.

## ALDEHYDS DERIVED FROM BIATOMIC ALCOHOLS.

Theoretically, all biatomic alcohols should give rise to two aldehyds, one formed by the elimination of $H^2$, and the other by the elimination of $H^4$. In reality, very few of these bodies are known.

**Aldehyds derived from Glycols by elimination of $H^2$.**—Three bodies of this class are known. They are: salicylic aldehyd ($C^7H^6O^2$), anisic aldehyd ($C^8H^8O^2$), and furfurol ($C^5H^4O^2$).

Salicylic aldehyd is a product of the oxidation of saligenin $C^7H^8O^2$, a body isomeric, but not identical with, benzoic glycol, still unknown.

Furfurol is produced by a very complicated reaction, when bran, saw-dust, etc., are distilled with dilute sulphuric acid, or with a solution of chloride of zinc.

Anisic aldehyd is formed in the oxidation of the oil of aniseed ($C^{10}H^{12}O$), according to the equation:

$$\underset{\text{Oil of aniseed.}}{(C^{10}H^{12}O)} + \underset{\text{Oxygen.}}{3\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\right)} = \underset{\text{Anisic aldehyd.}}{(C^8H^8O^2)} + \underset{\text{Oxalic acid.}}{(C^2H^2O^4)} + \underset{\text{Water.}}{(H^2O)}$$

These different aldehyds can each fix oxygen, and give rise to a biatomic and monobasic acid:

$$\underset{\text{Furfurol.}}{2\left(C^5H^4O^2\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} = \underset{\text{Pyromucic acid.}}{2\left(C^5H^4O^3\right)}$$

$$\underset{\text{Salicylic aldehyd.}}{2\left(C^7H^6O^2\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} = \underset{\text{Salicylic acid.}}{2\left(C^7H^6O^3\right)}$$

$$\underset{\text{Anisic aldehyd.}}{2\left(C^8H^8O^2\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} = \underset{\text{Anisic acid.}}{2\left(C^8H^8O^3\right)}$$

Two of these aldehyds, anisic and salicylic, can fix hydrogen and be converted, the first into anisic alcohol, the other into saligenin:

$$\underset{\text{Salicylic aldehyd.}}{\left(C^7H^6O^2\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}} = \underset{\text{Saligenin.}}{\left(C^7H^8O^2\right)}$$

$$\underset{\text{Anisic aldehyd.}}{\left(C^8H^8O^2\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}} = \underset{\text{Anisic alcohol.}}{\left(C^8H^{10}O^2\right)}$$

Furfurol has not yet been submitted to the action of nascent hydrogen, but M. Machuca and I have proved that, under the influence of an alcoholic solution of potash, it becomes resinous, instead of being transformed into a corresponding alcohol, as anisic aldehyd does.

We have seen that anisic alcohol is monomethylic paraoxybenzoic glycol; consequently, anisic aldehyd is the paraoxybenzoic aldehyd in which H is replaced by $CH^3$.

As to salicylic aldehyd, it is evidently isomeric with oxybenzoic and paraoxybenzoic aldehyd; when oxidized, it gives salicylic acid which is not identical either with oxybenzoic or with paraoxybenzoic acid.

Furfurol, salicylic aldehyd, and anisic aldehyd, all combine with ammonia, after the manner of the aromatic aldehyds derived from monatomic alcohols, that is to say, three molecules of these bodies unite with two molecules of ammonia, eliminating three $H^2O$:

$$\underset{\text{Furfurol.}}{3(C^5H^4O^2)} + \underset{\text{Ammonia.}}{2(NH^3)} = \underset{\text{Furfuramide.}}{(C^{15}H^{12}N^2O^3)} + \underset{\text{Water.}}{3(H^2O)}$$

The ammoniacal derivatives of anisic aldehyd and of furfurol may be converted into alkaloids, anisine and furfurine, which are isomeric with them. Anisine is produced when the ammoniacal derivative of anisic aldehyd is heated to 165°, and furfurine when furfuramide is submitted to the action of an alkaline solution. The ammoniacal derivative of salicylic aldehyd in no case undergoes such a transformation.

Salicylic aldehyd undergoes double decomposition with bases after the manner of acids, and gives salts called salicylites:

$$\underset{\text{Salicylic aldehyd.}}{\left(C^7H^6O^2\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic salicylite.}}{\left(C^7H^5KO^2\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

Anisic and salicylic aldehyds enter into double decomposition with the acid sulphites of the alkalies and produce, like the aldehyds of monatomic alcohols, crystallizable compounds which represent the acid sulphites the hydroxyl of which is replaced by the monatomic residues $\left(\left.\begin{matrix}C^7H^4O''\\H\end{matrix}\right\}O\right)'$ or $\left(\left.\begin{matrix}C^8H^6O''\\H\end{matrix}\right\}O\right)'$ derived from salicylic or anisic aldehyds by the subtraction of H:

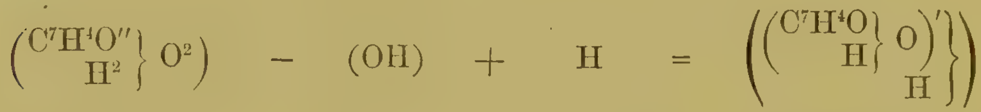
$$\underset{\text{Salicylic aldehyd.}}{\left(\left.\begin{matrix}\left(\left.\begin{matrix}C^7H^4O''\\H\end{matrix}\right\}O\right)'\\H\end{matrix}\right\}\right)} + \underset{\text{Acid sulphite of potassium.}}{\left(SO''\left\{\begin{matrix}OK\\OH\end{matrix}\right.\right)} = \underset{\text{Acid sulphite of salicyl-potassium.}}{\left(SO''\left\{\begin{matrix}OK\\\left(\left.\begin{matrix}C^7H^4O''\\H\end{matrix}\right\}O\right)'\end{matrix}\right.\right)}$$

$$+ \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

The action of bisulphites on furfurol has not yet been tried.

These aldehyds may be re-formed from their sulphurous combinations by heating these latter with water and an alkaline carbonate. One of them, the anisic, has been reproduced by the dry distillation of an intimate mixture of anisate and formiate of lime.

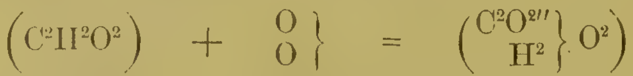
As to the constitution of these aldehyds, they should be considered as derived from the corresponding acids by the substitution of H for OH:



$$\left(\left.\begin{array}{r}C^7H^4O''\\H^2\end{array}\right\}O^2\right) - (OH) + H = \left(\left.\begin{array}{r}\left(\left.\begin{array}{r}C^7H^4O\\H\end{array}\right\}O\right)'\\H\end{array}\right\}\right)$$

Salicylic acid. Hydroxyl. Hydrogen. Salicylic aldehyd.

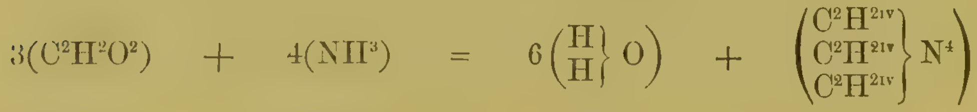
**Aldehyds derived from Glycols by elimination of $H^4$.**—While the preceding aldehyds combine with O, furnishing biatomic and monobasic acids, these unite with $O^2$ and furnish biatomic and bibasic acids:



$$(C^2H^2O^2) + \left.\begin{array}{c}O\\O\end{array}\right\} = \left(\left.\begin{array}{r}C^2O^{2''}\\H^2\end{array}\right\}O^2\right)$$

2nd aldehyd of glycol. Oxygen. Oxalic acid.

These aldehyds can combine with ammonia with elimination of water, and in this case a tertiary amide is produced:

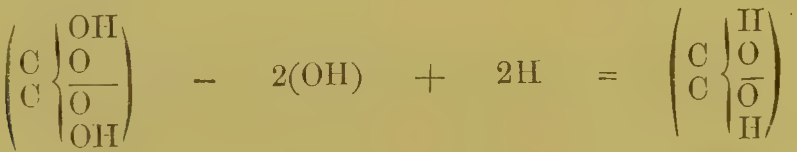


$$3(C^2H^2O^2) + 4(NH^3) = 6\left(\left.\begin{array}{c}H\\H\end{array}\right\}O\right) + \left(\left.\begin{array}{l}C^2H^{2\text{iv}}\\C^2H^{2\text{iv}}\\C^2H^{2\text{iv}}\end{array}\right\}N^4\right)$$

2nd aldehyd of glycol. Ammonia. Water. Glycosine.

As yet, only a single aldehyd of this group is known, that of ordinary glycol, which is called glyoxal, and the formula of which is $(C^2H^2O^2)$; and this has not been prepared from glycol, but from alcohol. It is only by examining its properties that its true nature has been established.

With regard to their constitution, it is probable that the aldehyds of this group are derived from their respective acids, like the preceding ones, by the substitution of H for OH. But in their case, the substitution would take place twice instead of once:



$$\left(\begin{array}{c}C\\C\end{array}\left\{\begin{array}{l}OH\\O\\\hline O\\OH\end{array}\right.\right) - 2(OH) + 2H = \left(\begin{array}{c}C\\C\end{array}\left\{\begin{array}{l}H\\O\\\hline O\\H\end{array}\right.\right)$$

Oxalic acid Glyoxal.

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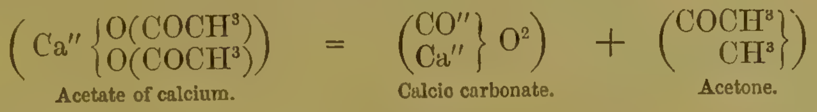
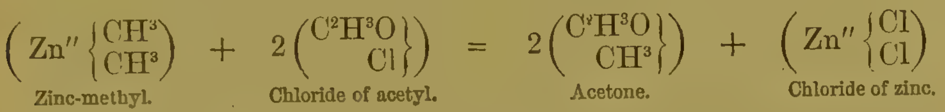
## ACETONES.

PREPARATION.—*First Process.*—These bodies may be prepared by the dry distillation of the calcic salts of monatomic acids:



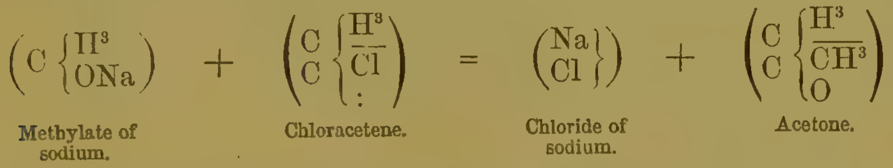
$$\underset{\text{Acetate of calcium.}}{\left(Ca''\left\{\begin{matrix}O(COCH^3)\\O(COCH^3)\end{matrix}\right.\right)} = \underset{\text{Calcic carbonate.}}{\left(\left.\begin{matrix}CO''\\Ca''\end{matrix}\right\}O^2\right)} + \underset{\text{Acetone.}}{\left(\left.\begin{matrix}COCH^3\\CH^3\end{matrix}\right\}\right)}$$

*Second Process.*—According to MM. Freund and Pebal, acetones may also be obtained by causing zinc-ethyl or zinc-methyl to act on the chlorides of acid radicles:



$$\underset{\text{Zinc-methyl.}}{\left(Zn''\left\{\begin{matrix}CH^3\\CH^3\end{matrix}\right.\right)} + 2\underset{\text{Chloride of acetyl.}}{\left(\left.\begin{matrix}C^2H^3O\\Cl\end{matrix}\right\}\right)} = 2\underset{\text{Acetone.}}{\left(\left.\begin{matrix}C^2H^3O\\CH^3\end{matrix}\right\}\right)} + \underset{\text{Chloride of zinc.}}{\left(Zn''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)}$$

*Third Process.*—M. Friedel has recently succeeded in preparing acetone by causing chloracetene to react with methylate of sodium:

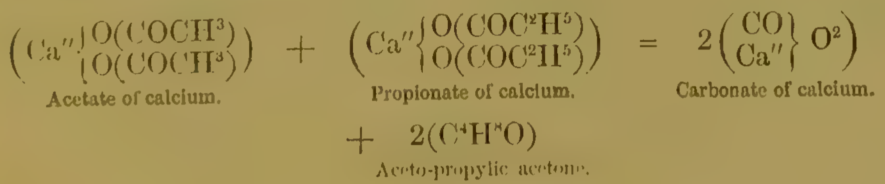


$$\underset{\text{Methylate of sodium.}}{\left(C\left\{\begin{matrix}H^3\\ONa\end{matrix}\right.\right)} + \underset{\text{Chloracetene.}}{\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\\overline{Cl}\\\vdots\end{matrix}\right.\right)} = \underset{\text{Chloride of sodium.}}{\left(\left.\begin{matrix}Na\\Cl\end{matrix}\right\}\right)} + \underset{\text{Acetone.}}{\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\\overline{CH^3}\\O\end{matrix}\right.\right)}$$

On substituting the formulæ of the homologues of the acetate of calcium for that of this acetate, in the equation given to explain the formation of acetone, it will be found that

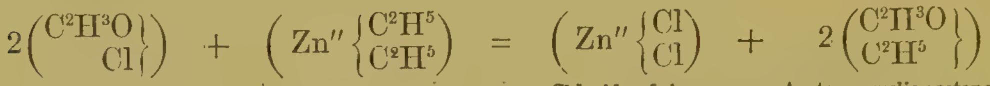
| the acids | give the | acetones |
|---|---|---|
| $C^2H^4O^2$ | . . . . . . . . . . | $C^3H^6O$ |
| $C^3H^6O^2$ | . . . . . . . . . . | $C^5H^{10}O$ |
| $C^4H^8O^2$ | . . . . . . . . . . | $C^7H^{14}O$ |
| $C^5H^{10}O^2$ | . . . . . . . . . . | $C^9H^{18}O$ |

It will be seen from this that two consecutive acetones differ, not by $(CH^2)$, like two adjoining terms of a homologous series, but by $2(CH^2)$. There ought therefore to exist an intermediate acetone between each two consecutive acetones: thus, between the acetone $(C^3H^6O)$ and propionic acetone $(C^5H^{10}O)$ there should exist another, answering to the formula $(C^4H^8O)$; such bodies are called mixed acetones. They are obtained by distilling an intimate mixture of the calcic salts of two consecutive acids:



$$\underset{\text{Acetate of calcium.}}{\left(Ca''\left\{\begin{matrix}O(COCH^3)\\O(COCH^3)\end{matrix}\right.\right)} + \underset{\text{Propionate of calcium.}}{\left(Ca''\left\{\begin{matrix}O(COC^2H^5)\\O(COC^2H^5)\end{matrix}\right.\right)} = 2\underset{\text{Carbonate of calcium.}}{\left(\left.\begin{matrix}CO\\Ca''\end{matrix}\right\}O^2\right)}$$
$$+ \underset{\text{Aceto-propylic acetone.}}{2(C^4H^8O)}$$

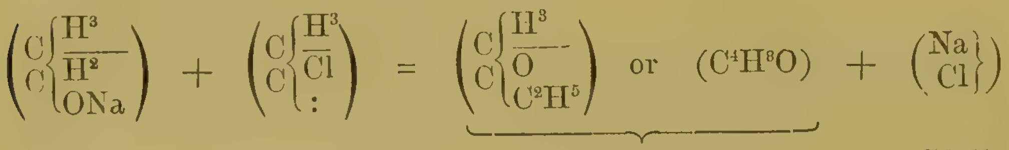
Similar acetones may also be prepared by MM. Freund and Pebal's process:



$$2\left(\left.\begin{matrix}C^2H^3O\\ \quad Cl\end{matrix}\right\}\right) + \left(Zn''\left\{\begin{matrix}C^2H^5\\ C^2H^5\end{matrix}\right.\right) = \left(Zn''\left\{\begin{matrix}Cl\\ Cl\end{matrix}\right.\right) + 2\left(\left.\begin{matrix}C^2H^3O\\ C^2H^5\end{matrix}\right\}\right)$$

Chloride of acetyl. Zinc-ethyl. Chloride of zinc. Aceto-propylic acetone.

Probably they could also be obtained by Friedel's process, if chloracetene were made to act, not on the methylate, but on the ethylate or amylate of sodium:



$$\left(\begin{matrix}C\\ C\end{matrix}\left\{\begin{array}{l}H^3\\ \hline H^2\\ ONa\end{array}\right.\right) + \left(\begin{matrix}C\\ C\end{matrix}\left\{\begin{array}{l}H^3\\ \hline Cl\\ :\end{array}\right.\right) = \underbrace{\left(\begin{matrix}C\\ C\end{matrix}\left\{\begin{array}{l}H^3\\ \hline O\\ C^2H^5\end{array}\right.\right) \text{ or } (C^4H^8O)} + \left(\left.\begin{matrix}Na\\ Cl\end{matrix}\right\}\right)$$

Sodic ethylate. Chloracetene. Aceto-propylic acetone. Chloride of sodium.

Properties.—Though a certain number of acetones are known, yet only the properties of acetone proper have been much studied. We will therefore speak of these; probably they also appertain to the other bodies of the same class.

1st. Oxidizing agents do not fix oxygen on acetone; which property clearly distinguishes it from the aldehyds.

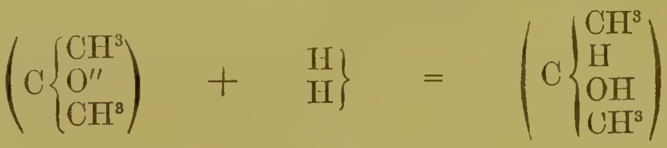
2nd. Nascent hydrogen transforms acetone into a compound which contains two additional atoms of hydrogen:

$$(C^3H^6O) + H^2 = (C^3H^8O)$$

Acetone. Hydrogen. Isopropylic alcohol.

This new body is not, however, identical with the alcohol possessing the same composition. In reality, the alcohols give aldehyds on oxidation, while the body in question reproduces the original acetone.

We have already seen, when speaking of alcohols, that isopropylic alcohol is a secondary alcohol, that is to say, an alcohol formed by an atom of carbon, one atomicity of which being united to an hydroxyl and another to hydrogen, the two remaining are joined to the other carbons, as the following equation shows:



$$\left(C\left\{\begin{matrix}CH^3\\ O''\\ CH^3\end{matrix}\right.\right) + \left.\begin{matrix}H\\ H\end{matrix}\right\} = \left(C\left\{\begin{matrix}CH^3\\ H\\ OH\\ CH^3\end{matrix}\right.\right)$$

Acetone. Hydrogen. Isopropylic alcohol.

At the same time as the acetone fixes hydrogen, a portion of it is doubled, also being hydrogenized, and is transformed into a compound which perhaps acts as a biatomic alcohol, pinakone:

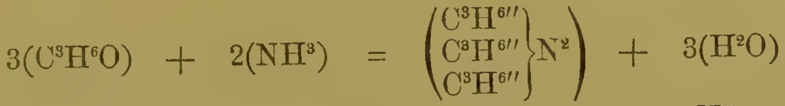
$$2(C^3H^6O) + H^2 = (C^6H^{14}O^2)$$

Acetone. Hydrogen. Pinakone.

3rd. Under the simultaneous action of hydrocyanic acid, water, and hydrochloric acid, acetone is transformed into an acid which is isomeric or identical with oxybutyric acid:

$$\underset{\text{Acetone.}}{(C^3H^6O)} + \underset{\text{Hydrocyanic acid.}}{(CNH)} + \underset{\text{Water.}}{2(H^2O)} + \underset{\text{Hydrochloric acid.}}{(HCl)} = \underset{\text{Acetonic acid.}}{(C^4H^8O^3)} + \underset{\text{Chloride of ammonium.}}{(NH^4Cl)}$$

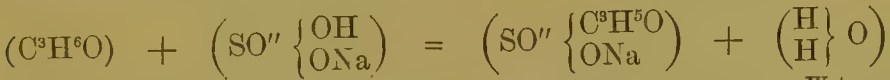
4th. Heated to 100° with ammonia, acetone combines with this body, water being eliminated, and a base is produced, acetonine, which is to acetone what amarine (an isomer of hydrobenzamide) is to benzoic aldehyd:



$$\underset{\text{Acetone.}}{3(C^3H^6O)} + \underset{\text{Ammonia.}}{2(NH^3)} = \underset{\text{Acetonine.}}{\left(\left.\begin{matrix}C^3H^{6''}\\C^3H^{6''}\\C^3H^{6''}\end{matrix}\right\}N^2\right)} + \underset{\text{Water.}}{3(H^2O)}$$

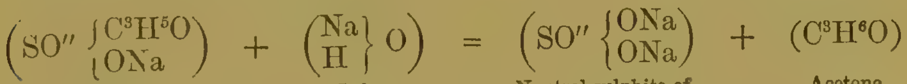
5th. Aniline does not combine with acetone, a property distinguishing this body from the aldehyds.

6th. The acid sulphite of sodium acts with acetone as with the aldehyds: crystallizable compounds, soluble in water, are produced:



$$\underset{\text{Acetone.}}{(C^3H^6O)} + \underset{\text{Acid sulphite of sodium.}}{\left(SO''\left\{\begin{matrix}OH\\ONa\end{matrix}\right.\right)} = \underset{\text{Acid sulphite containing the elements of acetone.}}{\left(SO''\left\{\begin{matrix}C^3H^5O\\ONa\end{matrix}\right.\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

These compounds, treated by alkalies, give a neutral sulphite and the acetone again becomes free:



$$\underset{\text{Acid sulphite containing the elements of acetone.}}{\left(SO''\left\{\begin{matrix}C^3H^5O\\ONa\end{matrix}\right.\right)} + \underset{\text{Soda.}}{\left(\left.\begin{matrix}Na\\H\end{matrix}\right\}O\right)} = \underset{\text{Neutral sulphite of sodium.}}{\left(SO''\left\{\begin{matrix}ONa\\ONa\end{matrix}\right.\right)} + \underset{\text{Acetone.}}{(C^3H^6O)}$$

7th. Dehydrating agents cause acetone to lose a molecule of water. The carbide of hydrogen $(C^3H^4)$ ought to be thereby produced, but it is a polymer of this hydrocarbide, mesitylene $(C^9H^{12}) = 3(C^3H^4)$, which is really obtained.

8th. Chlorine and bromine give substitution-products with acetone.

9th. The pentachloride of phosphorus yields two atoms of chlorine to acetone in exchange for its atom of oxygen. A chlorinated body is thereby produced which corresponds to the formula $(C^3H^6Cl^2)$:

$$\underset{\text{Acetone.}}{(C^3H^6O'')} + \underset{\text{Pentachloride of phosphorus.}}{(PCl^5)} = \underset{\text{Oxychloride of phosphorus.}}{(PCl^3O)} + \underset{\text{Chloride derived from acetone.}}{(C^3H^6Cl^2)}$$

This chloride is isomeric with the chloride of propylene, from which it differs by its boiling point; but treated by an alcoholic solution of potash, it gives rise to chlorinated propylene perfectly identical with that derived from propylene:

$$\underset{\substack{\text{Chloride derived}\\ \text{from acetone.}}}{(C^3H^6Cl^2)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\ H\end{matrix}\right\}O\right)} = \underset{\substack{\text{Chloride}\\ \text{of potassium.}}}{\left.\begin{matrix}K\\ Cl\end{matrix}\right\}} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)} + \underset{\substack{\text{Chlorinated}\\ \text{propylene.}}}{(C^3H^5Cl)}$$

When hydrochloric acid acts on acetone, a body is produced which also corresponds to the formula $(C^3H^5Cl)$. This is called chloride of mesityl, and appears to be a simple isomer of the preceding: when treated with an alcoholic solution of potash, it is transformed into oxide of mesityl $(C^6H^{10}O)$:

$$\underset{\text{Chloride of mesityl.}}{2(C^3H^5Cl)} + \underset{\text{Potash.}}{2\left(\left.\begin{matrix}K\\ H\end{matrix}\right\}O\right)} = \underset{\substack{\text{Chloride of}\\ \text{potassium.}}}{2\left(\left.\begin{matrix}K\\ Cl\end{matrix}\right\}\right)} + \underset{\text{Oxide of mesityl.}}{\left(\left.\begin{matrix}C^3H^5\\ C^3H^5\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)}$$

M. Friedel's chloride in this case loses (HCl) and gives allylene:

$$\underset{\substack{\text{Chlorinated}\\ \text{propylene.}}}{(C^3H^5Cl)} = \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{(HCl)} + \underset{\text{Allylene.}}{(C^3H^4)}$$

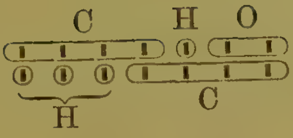
10. When acetone in vapour is transmitted over potassium, there is formed, according to the temperature, either carbonate of potassium and marsh gas, or acetate and formiate of potassium, with hydrogen:

$$\underset{\text{Acetone.}}{\left(CO''\left\{\begin{matrix}CH^3\\ CH^3\end{matrix}\right.\right)} + \underset{\text{Potash.}}{2\,(KO.H)} = \underset{\text{Potassic carbonate.}}{\left(CO''\left\{\begin{matrix}OK\\ OK\end{matrix}\right.\right)} + \underset{\substack{\text{Hydride of}\\ \text{methyl (marsh gas).}}}{2(CH^4)}$$

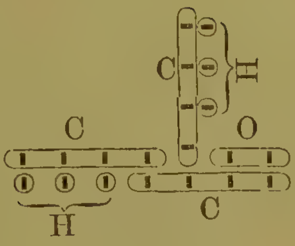
$$\underset{\text{Acetone.}}{(C^3H^6O)} + \underset{\text{Potash.}}{2\left(\left.\begin{matrix}K\\ H\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)} = \underset{\text{Potassic acetate.}}{\left(\left.\begin{matrix}C^2H^3O\\ K\end{matrix}\right\}O\right)}$$

$$+ \underset{\text{Potassic formiate.}}{\left(\left.\begin{matrix}CHO\\ K\end{matrix}\right\}O\right)} + \underset{\text{Hydrogen.}}{3\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}\right)}$$

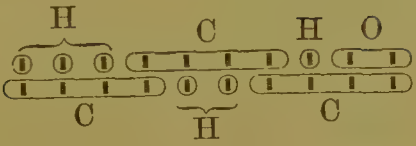
CONSTITUTION.—Acetones are isomeric with the aldehyds of a higher series than their own, and with certain alcohols. Ordinary acetone $(C^3H^6O)$ has the same composition as propionic aldehyd and allylic alcohol, but its mode of formation well explains its isomerism with these bodies. In reality the acetones are only aldehyds less carburetted than those of which they are isomers, and in which the atom of hydrogen which was in juxtaposition to oxygen has been replaced by an alcohol radicle:



Acetic aldehyd.



Ordinary acetone.

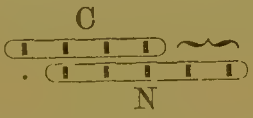


Propylic aldehyd (isomeric with acetone).

The synthetical process of preparation discovered by MM. Freund and Pebal leads us to suppose that there are numerous cases of isomerism among the acetones; it is not probable that the body obtained by the action of chloride of acetyl on zinc-ethyl is identical with that arising from the action of chloride of propyl on zinc-methyl.

## CYANOGEN COMPOUNDS.

Nitrogen, being generally trivalent though it is pentatomic, and carbon being tetratomic, the three units of atomicity which act in an atom of nitrogen may saturate three of the units of an atom of carbon, the fourth remaining free; therefore the radicle CN is triatomic and monovalent, as the following figure shows:



This radicle is named cyanogen, and may be regarded as a compound radicle to be classed by the side of the halogen metalloids (chlorine, bromine, iodine, and fluorine). Its compounds are very important, and to render their formulæ less complicated, it is represented by the symbol $Cy = CN$.

Free cyanogen, like chlorine, bromine, and iodine, has a double molecule corresponding to the formula $\left.\begin{matrix}Cy\\Cy\end{matrix}\right\}$; if, in this molecule, an atom of hydrogen or an atom of a metal be substituted for a group CN, hydrocyanic acid $\left(\left.\begin{matrix}CN\\H\end{matrix}\right\}\right)$ or a metallic cyanide $\left(\left.\begin{matrix}CN\\M'\end{matrix}\right\}\right)$ is obtained. If the cyanogen be replaced by chlorine, bromine, or iodine, the chloride, bromide, or iodide of cyanogen is produced:

$$\left.\begin{matrix}Cy\\Cl\end{matrix}\right\} \qquad \left.\begin{matrix}Cy\\Br\end{matrix}\right\} \qquad \left.\begin{matrix}Cy\\I\end{matrix}\right\}$$

Cyanogen may also be substituted for a part or the whole of the hydrogen contained in water and its congeners, hydrosulphuric, hydroselenic, and hydrotelluric acids; thence we have cyanic acid $\left(\left.\begin{matrix}\mathrm{Cy}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)$, cyanic anhydride $\left(\left.\begin{matrix}\mathrm{Cy}\\\mathrm{Cy}\end{matrix}\right\}\mathrm{O}\right)^*$, hydrosulpho-cyanic, or better, sulphocyanic acid $\left(\left.\begin{matrix}\mathrm{Cy}\\\mathrm{H}\end{matrix}\right\}\mathrm{S}\right)$, sulphocyanic anhydrosulphide $\left(\left.\begin{matrix}\mathrm{Cy}\\\mathrm{Cy}\end{matrix}\right\}\mathrm{S}\right)^*$, hydroselenio-cyanic, or selenio-cyanic acid $\left(\left.\begin{matrix}\mathrm{Cy}\\\mathrm{H}\end{matrix}\right\}\mathrm{Se}\right)$, selenio-cyanic anhydroselenide $\left(\left.\begin{matrix}\mathrm{Cy}\\\mathrm{Cy}\end{matrix}\right\}\mathrm{Se}\right)^*$; and finally, tellurocyanic acid $\left(\left.\begin{matrix}\mathrm{Cy}\\\mathrm{H}\end{matrix}\right\}\mathrm{Te}\right)^*$, and tellurocyanic anhydrotelluride $\left(\left.\begin{matrix}\mathrm{Cy}\\\mathrm{Cy}\end{matrix}\right\}\mathrm{Te}\right)^*$.

Those of the above compounds which are marked with an asterisk are unknown.

Sulphuretted, oxygenized, etc., compounds of cyanogen, corresponding to oxygenized water $\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}^2\right)$, may also possibly exist.

It is thus that the constitution of persulphohydrocyanic acid $(\mathrm{Cy^2H^2S^3})$ and persulphocyanogen $(\mathrm{Cy^3HS^3})$ may be accounted for. The first of these bodies may be regarded as a combination of hydrosulphuric acid and bisulphide of cyanogen, and the second as resulting from the substitution of Cy for H in the first.

| | |
|---|---|
| Persulphohydrocyanic acid . . . . | $\left(\left.\begin{matrix}\mathrm{Cy}\\\mathrm{Cy}\end{matrix}\right\}\mathrm{S}^2,\ \left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{S}\right)$ |
| Persulphocyanogen . . . . . . . . | $\left(\left.\begin{matrix}\mathrm{Cy}\\\mathrm{Cy}\end{matrix}\right\}\mathrm{S}^2,\ \left.\begin{matrix}\mathrm{Cy}\\\mathrm{H}\end{matrix}\right\}\mathrm{S}\right)$ |

Cyanogen may also be substituted for a part or the whole of the hydrogen of ammonia. The compounds thus formed are:

| | |
|---|---|
| Cyanamide. . . . . . . . | $\left(\left.\begin{matrix}\mathrm{Cy}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{N}\right)$ |
| Dicyanamide . . . . . . . | $\left(\left.\begin{matrix}\mathrm{Cy}\\\mathrm{Cy}\\\mathrm{H}\end{matrix}\right\}\mathrm{N}\right)$ |
| and tricyanamide . . . . . . | $\left(\left.\begin{matrix}\mathrm{Cy}\\\mathrm{Cy}\\\mathrm{Cy}\end{matrix}\right\}\mathrm{N}\right)$ |

It may also replace either the hydrogen or the hydroxyl in polyatomic alcohols, and give rise to cyanhydrins which are perfectly analogous to the chlorhydrins and bromhydrins.

Thus to glycol $\left(\mathrm{C^2H^{4''}}\left\{\begin{matrix}\mathrm{OH}\\\mathrm{OH}\end{matrix}\right.\right)$ there correspond: the cyanhydrin $\left(\mathrm{C\ H^{4''}}\left\{\begin{matrix}\mathrm{OH}\\\mathrm{Cy}\end{matrix}\right.\right)$, and dicyanhydrin or cyanide of ethylene $\left(\mathrm{C^2H^{4''}}\left\{\begin{matrix}\mathrm{Cy}\\\mathrm{Cy}\end{matrix}\right.\right)$.

But the history of cyanogen compounds does not stop here. They possess the singular property of giving rise to a great number of polymers. To free cyanogen there corresponds a black body, paracyanogen, whose degree of condensation is not known, but which is a polymer of cyanogen $\left.\begin{matrix}\mathrm{Cy}''\\ \mathrm{Cy}''\end{matrix}\right\}$. No polymer of hydrocyanic acid is known, but the cyanides possess the property of giving rise to double cyanides. Among these bodies there are some which are similar to double chlorides, but there are others differing in character from these salts, and which appear to result, not from the juxtaposition of two molecules, but from a true atomic combination constituting condensed cyanides $\left.\begin{matrix}\mathrm{Cy}''\\ \mathrm{M}''\end{matrix}\right\}$. Thus a solid chloride ($\mathrm{Cy^3Cl^3}$) whose condensation is triple, corresponds to the liquid chloride (CyCl), of which latter a gaseous modification appears also to exist at the ordinary temperature. Condensed bromides and iodides of cyanogen are not as yet known, but to cyanic acid $\left(\left.\begin{matrix}\mathrm{Cy}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)$ there correspond dicyanic acid $\left(\left.\begin{matrix}\mathrm{Cy}^2\\ \mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right)$ and tricyanic or cyanuric acid $\left(\left.\begin{matrix}\mathrm{Cy}^3\\ \mathrm{H}^3\end{matrix}\right\}\mathrm{O}^3\right)$. Besides these, there exists a body called cyamelid, which is also a polymer of cyanic acid, but whose degree of condensation is unknown.

To cyanamide there corresponds a polymer, melamine and its isomer, melam, $\left(\mathrm{Cy}^3\left\{\begin{matrix}\mathrm{NH}^2\\ \mathrm{NH}^2\\ \mathrm{NH}^2\end{matrix}\right.\right)$; this triamide may be converted, by means of the alkalies, into cyanuric acid and ammonia, 3(OH) being substituted for $3(\mathrm{NH}^2)$; but this substitution may take place partially: thence ammeline $\left(\mathrm{Cy}^3\left\{\begin{matrix}\mathrm{NH}^2\\ \mathrm{NH}^2\\ \mathrm{OH}\end{matrix}\right.\right)$, ammelid and $\left(\mathrm{Cy}^3\left\{\begin{matrix}\mathrm{NH}^2\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\right.\right)$ sulpho-mellonic acid $\left(\mathrm{Cy}^3\left\{\begin{matrix}\mathrm{NH}^2\\ \mathrm{SH}\\ \mathrm{SH}\end{matrix}\right.\right)$, can also be produced by introducing the group SH in place of the group OH; and, lastly, $(\mathrm{NH}^2)$ may be replaced by Cl, chloro-cyanamide $\left(\mathrm{Cy}^3\left\{\begin{matrix}\mathrm{NH}^2\\ \mathrm{NH}^2\\ \mathrm{Cl}\end{matrix}\right.\right)$ being obtained by this substitution.

To dicyanamide $\left(\left.\begin{matrix}\mathrm{Cy}^2\\ \mathrm{H}\end{matrix}\right\}\mathrm{N}\right)$ there correspond hydromellon $\left((\mathrm{Cy}^2)^3\left\{\begin{matrix}(\mathrm{NH})''\\ (\mathrm{NH})''\\ (\mathrm{NH})''\end{matrix}\right.\right)$, and cyameluric acid, $\left((\mathrm{Cy}^2)^3\left\{\begin{matrix}(\mathrm{NH})''\\ (\mathrm{NH})''\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\right.\right)$ or $\left((\mathrm{Cy}^2)^3\left\{\begin{matrix}\mathrm{N}'''\\ \mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\right.\right)$ according as the formula ($\mathrm{C^6H^3N^7O^3}$) given by Liebig, or that proposed by Gerhardt ($\mathrm{C^6H^4N^8O^2}$) for this body, be adopted.

Tricyanamide is unknown.

The triatomicity of cyanogen has been proved by the experiments of M. Gauthier, as also by those of M. Gal. These chemists have each shown that the greater part of cyanogen compounds, hydrocyanic acid, hydrocyanic and cyanic ethers, can fix HCl, HBr, or HI in the same way as ammonia, and give crystallizable compounds.

**Free Cyanogen.**—This body may be obtained by the dehydration of oxamide:

$$\underset{\text{Oxamide.}}{\left(\left.\begin{matrix}C^2O^{2\prime\prime}\\ H^4\end{matrix}\right\}N^2\right)} = \underset{\text{Water.}}{2(H^2O)} + \underbrace{(C^2N^2) = \left.\begin{matrix}CN\\ CN\end{matrix}\right\} = \left.\begin{matrix}Cy\\ Cy\end{matrix}\right\}}_{\text{Free cyanogen.}}$$

It is usually prepared by the dry distillation of mercuric cyanide:

$$\underset{\substack{\text{Mercuric}\\ \text{cyanide.}}}{\left.\begin{matrix}Hg^{\prime\prime}\\ Cy^2\end{matrix}\right\}} = \underset{\text{Mercury.}}{Hg} + \underset{\text{Cyanogen.}}{\left.\begin{matrix}Cy\\ Cy\end{matrix}\right\}}$$

In this operation a black residue is always formed, which has the same composition as cyanogen, and which is entirely converted into this body, when heated in an inert gas; it is paracyanogen $\left.\begin{matrix}Cy^{n}\\ Cy^{n}\end{matrix}\right\}$.

Cyanogen is gaseous at the ordinary temperature; it liquefies between −25° and −30°; below −34° it is solid. It is slightly soluble in water, and more so in alcohol. Heated with an alkaline metal, it gives a metallic cyanide:

$$\underset{\text{Cyanogen.}}{\left.\begin{matrix}Cy\\ Cy\end{matrix}\right\}} + \underset{\text{Potassium.}}{\left.\begin{matrix}K\\ K\end{matrix}\right\}} = \underset{\substack{\text{Cyanide of}\\ \text{potassium.}}}{2\left(\left.\begin{matrix}K\\ Cy\end{matrix}\right\}\right)}$$

In presence of caustic potash, it gives rise to a mixture of cyanide and cyanate, in the same way as chlorine gives a mixture of chloride and hypochlorite:

$$\underset{\text{Cyanogen.}}{\left.\begin{matrix}Cy\\ Cy\end{matrix}\right\}} + \underset{\text{Potash.}}{2\left(\left.\begin{matrix}K\\ H\end{matrix}\right\}O\right)} = \underset{\substack{\text{Cyanide of}\\ \text{potassium.}}}{\left.\begin{matrix}K\\ Cy\end{matrix}\right\}} + \underset{\substack{\text{Cyanate of}\\ \text{potassium.}}}{\left(\left.\begin{matrix}Cy\\ K\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)}$$

Cyanogen unites directly with several organic alkalies, furnishing new alkaloids. Oxalic acid is always obtained among the products of the decomposition of these cyanogenized alkalies, which can be readily understood, as cyanogen represents the oxalate of ammonium, less water.

It can also unite directly with one or with two molecules of hydrosulphuric acid, giving the compounds $\left(\left.\begin{matrix}Cy\\ Cy\end{matrix}\right\}, \left.\begin{matrix}H\\ H\end{matrix}\right\}S\right)$ or $\left(\left.\begin{matrix}Cy\\ Cy\end{matrix}\right\}, \left.\begin{matrix}H^2\\ H^2\end{matrix}\right\}S^2\right)$.

**Hydrocyanic Acid.**—The best method of obtaining pure hydrocyanic acid consists in transmitting a current of perfectly dry sulphuretted hydrogen gas through a tube full of dry cyanide of mercury heated in a sand-bath. The acid disengaged is collected in a cold receiver:

$$\underset{\text{Mercuric cyanide.}}{\left.\begin{matrix}\text{Hg}''\\ \text{Cy}^2\end{matrix}\right\}} + \underset{\text{Hydrosulphuric acid.}}{\left(\left.\begin{matrix}\text{H}\\ \text{H}\end{matrix}\right\}\text{S}\right)} = \underset{\text{Mercuric sulphide.}}{(\text{Hg}''\text{S})} + \underset{\text{Hydrocyanic acid.}}{2\left(\left.\begin{matrix}\text{H}\\ \text{Cy}\end{matrix}\right\}\right)}$$

As the decomposition of the mercuric cyanide takes place, the contents of the tube become black. In order that the acid obtained be pure, the operation should be arrested while there still remains some cyanide undecomposed, that is to say white, in the anterior part of the tube; without this precaution, a little hydrosulphuric acid might be dissolved in the hydrocyanic acid.

Hydrocyanic, called also Prussic acid, is the strongest poison known; one drop is sufficient to kill a dog, and its effects are instantaneous.

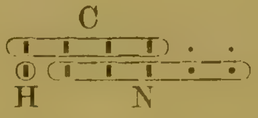
Hydrocyanic acid boils at 26°·5; it congeals in the freezing mixture formed by ice and sea salt; its density at 18° is ·6967. It is very difficult to preserve the anhydrous acid, especially in the light, but if it be diluted with water, and especially if mixed with mineral acids, it keeps much better. Its spontaneous decomposition appears to be owing to some impurities, for when absolutely pure, it may be preserved. The products of its decomposition have not been much studied.

In presence of potash and a ferrous salt mixed with a certain quantity of ferric salt, hydrocyanic acid gives a blue precipitate which generally remains mixed with the mixed hydrates of iron precipitated at the same time; but if hydrochloric acid be added, the hydrates of iron are dissolved and a very pure blue precipitate remains, which shows the presence of Prussic acid.

Under the influence of hydrating agents such as potash, sulphuric, or dilute hydrochloric acid, hydrocyanic acid absorbs water and formiate of ammonium is obtained, or rather the products of the decomposition of this salt by the reagent employed:

$$\underset{\text{Hydrocyanic acid.}}{\left(\left.\begin{matrix}\text{CN}\\ \text{H}\end{matrix}\right\}\right)} + \underset{\text{Water.}}{2(\text{H}^2\text{O})} = \underset{\text{Formiate of ammonium.}}{\left(\left.\begin{matrix}\text{CHO}\\ \text{NH}^4\end{matrix}\right\}\text{O}\right)}$$

M. Gauthier has observed that hydrocyanic acid combines directly with hydriodic and with hydrochloric acids,* giving the crystallizable compounds (CNH.HI) and (CNH.HCl). These combinations are readily explained. Hydrocyanic acid being, according to our hypothesis,



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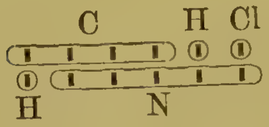
* This has not been published, but M. Gauthier has communicated it to me privately.

its hydrochlorate is



**Metallic Cyanides.**—Hydrocyanic acid may exchange its hydrogen for a metal, and give rise to cyanides which contain as many atoms of the radicle cyanogen as are equal to the number which expresses the value of substitution of the metal in the compound formed.

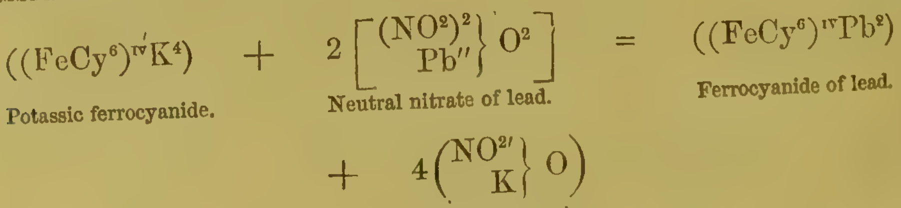
Metallic cyanides unite among themselves to form double cyanides. These are often true double cyanides, in which the two constituent metals may be detected by means of appropriate reagents; such are the double cyanides of potassium and cadmium, of potassium and silver, etc.

Sometimes they are compounds in which one of the metals cannot be detected by its ordinary tests unless the molecule be decomposed. In this latter case it is supposed that one of the metals is joined with cyanogen to constitute a compound radicle with which the other metal is united. Such bodies are designated by a name which, while indicating their composition, prevents their being considered as double cyanides. Thus we say: cuprocyanide of potassium, ferrocyanide of sodium, platinocyanide of ammonium.

The principal compounds of this order are the ferricyanides, the ferrocyanides, cobalticyanides, nickelocyanides, cuprocyanides, and platinocyanides. The most important are the ferrocyanides and the ferricyanides.

**Ferrocyanides.**—When a ferric salt is precipitated by an excess of alkaline cyanide, a precipitate is formed which redissolves. On evaporation, the liquid deposits beautiful yellow crystals of a compound called ferrocyanide of potassium, cyanoferride of potassium, yellow prussiate of potash, etc. These crystals correspond to the formula $(Fe''Cy^2,4KCy+6aq.)$. However, this formula, in which the salt is considered as a double cyanide, is objectionable, and the formula $((FeCy^6)^{iv}K^4+6aq.)$, in which potassium is considered as united to the tetratomic radicle $(FeCy^6)$, should be substituted for it.

The ferrocyanide of potassium is neutral; it is not poisonous and is readily soluble in water; its solution is precipitated by most metallic solutions, compounds being thereby formed which are derived from the potassic ferrocyanide by the substitution of another metal for the potassium:

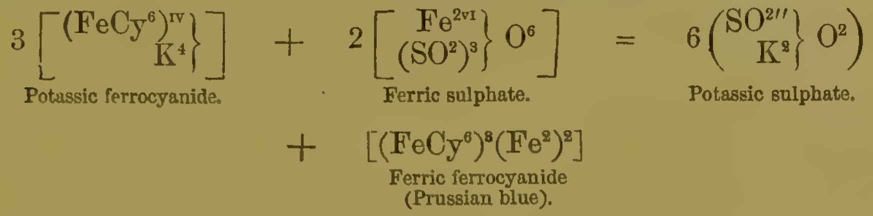


$$((FeCy^6)^{iv}K^4) + 2\left[\left.\begin{matrix}(NO^2)^2\\ Pb''\end{matrix}\right\}O^2\right] = ((FeCy^6)^{iv}Pb^2) + 4\left(\left.\begin{matrix}NO^{2\prime}\\ K\end{matrix}\right\}O\right)$$

Potassic ferrocyanide. Neutral nitrate of lead. Ferrocyanide of lead. Nitrate of potassium.

Treated with hydrochloric acid, yellow prussiate of potash exchanges its potassium for hydrogen, and white crystalline scales of hydroferrocyanic acid ($((\mathrm{FeCy}^6)^{\mathrm{iv}}\mathrm{H}^4)$) are obtained.

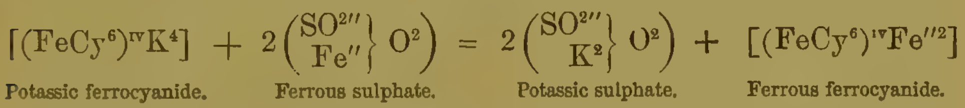
If a solution of ferrocyanide of potassium or hydroferrocyanic acid be added to a solution of a ferric salt, a blue precipitate (Prussian blue) is formed. In order to understand the constitution of such a body, we should consider that ferric salts contain a double atom of iron, $\mathrm{Fe}^2$, acting as a hexatomic radicle. As this double atom cannot be substituted for less than six atoms of potassium, and as potassic ferrocyanide only contains four, the reaction takes place between three molecules of ferrocyanide and two of the ferric salt:



$$\underset{\text{Potassic ferrocyanide.}}{3\left[\left.\begin{matrix}(\mathrm{FeCy}^6)^{\mathrm{iv}}\\ \mathrm{K}^4\end{matrix}\right\}\right]} + \underset{\text{Ferric sulphate.}}{2\left[\left.\begin{matrix}\mathrm{Fe}^{2\mathrm{vi}}\\ (\mathrm{SO}^2)^3\end{matrix}\right\}\mathrm{O}^6\right]} = \underset{\text{Potassic sulphate.}}{6\left(\left.\begin{matrix}\mathrm{SO}^{2''}\\ \mathrm{K}^2\end{matrix}\right\}\mathrm{O}^2\right)}$$

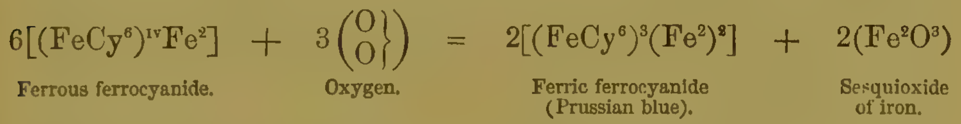
$$+ \underset{\text{(Prussian blue).}}{\underset{\text{Ferric ferrocyanide}}{[(\mathrm{FeCy}^6)^3(\mathrm{Fe}^2)^2]}}$$

When the ferric salt is replaced in this process by a ferrous salt, the reaction takes place between one molecule of ferrocyanide and two of the ferrous salt, and a ferrous ferrocyanide is formed:



$$\underset{\text{Potassic ferrocyanide.}}{[(\mathrm{FeCy}^6)^{\mathrm{iv}}\mathrm{K}^4]} + \underset{\text{Ferrous sulphate.}}{2\left(\left.\begin{matrix}\mathrm{SO}^{2''}\\ \mathrm{Fe}''\end{matrix}\right\}\mathrm{O}^2\right)} = \underset{\text{Potassic sulphate.}}{2\left(\left.\begin{matrix}\mathrm{SO}^{2''}\\ \mathrm{K}^2\end{matrix}\right\}\mathrm{O}^2\right)} + \underset{\text{Ferrous ferrocyanide.}}{[(\mathrm{FeCy}^6)^{\mathrm{iv}}\mathrm{Fe}''^2]}$$

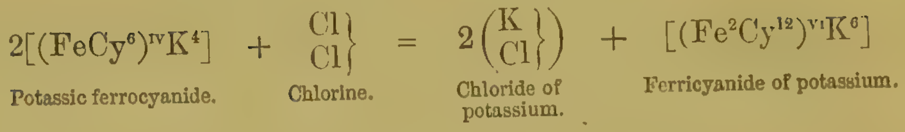
On contact with air, ferrous ferrocyanide is transformed into a mixture of Prussian blue and sesquioxide of iron:



$$\underset{\text{Ferrous ferrocyanide.}}{6[(\mathrm{FeCy}^6)^{\mathrm{iv}}\mathrm{Fe}^2]} + \underset{\text{Oxygen.}}{3\left(\left.\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\}\right)} = \underset{\text{(Prussian blue).}}{\underset{\text{Ferric ferrocyanide}}{2[(\mathrm{FeCy}^6)^3(\mathrm{Fe}^2)^2]}} + \underset{\text{of iron.}}{\underset{\text{Sesquioxide}}{2(\mathrm{Fe}^2\mathrm{O}^3)}}$$

In manufactures, Prussian blue is always prepared in this manner. Therefore, when it is wished to procure this body in a pure state from the Prussian blue of commerce, this latter should be powdered and treated with hydrochloric acid, in order to dissolve the ferric oxide it contains.

**Ferricyanides.**—By the action of a current of chlorine on a solution of potassic ferrocyanide, chloride of potassium is produced and a new body of a red colour which is separated from the potassic chloride by repeated crystallizations. This new body is called red prussiate of potash, ferricyanide of potassium, cyanoferride of potassium, etc.; its formula, regarding it as a double cyanide, would be $[(\mathrm{Fe}^2\mathrm{Cy}^6),6\mathrm{KCy}]$; but it should be written $[(\mathrm{Fe}^2\mathrm{Cy}^{12})^{\mathrm{vi}}\mathrm{K}^6]$, and be regarded as resulting from the union of potassium with the hexatomic radicle ferricyanogen $(\mathrm{Fe}^2\mathrm{Cy}^{12})^{\mathrm{vi}}$. The reaction which gives rise to this salt is expressed by the following equation:



$$\underset{\text{Potassic ferrocyanide.}}{2[(\mathrm{FeCy^6})^{\mathrm{IV}}\mathrm{K^4}]} + \underset{\text{Chlorine.}}{\left.\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right\}} = \underset{\text{Chloride of potassium.}}{2\left(\left.\begin{matrix}\mathrm{K}\\\mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\text{Ferricyanide of potassium.}}{[(\mathrm{Fe^2Cy^{12}})^{\mathrm{VI}}\mathrm{K^6}]}$$

It will be seen that in this reaction two molecules of a tetratomic ferrocyanogen radicle have united, exchanging two atomicities, and have produced the hexatomic group $(\mathrm{Fe^2Cy^{12}}) = 2(\mathrm{FeCy^6})$.

Potassic ferricyanide exchanges its potassium for other metals by double decomposition. If iron be thus substituted, a blue insoluble body is obtained, having for formula $[(\mathrm{Fe^2Cy^{12}})\mathrm{Fe^3}]$, and called Turnbull's blue. This blue precipitate, which is formed when a ferrous salt is precipitated by potassic ferricyanide, should not be confounded with Prussian blue, which is formed by the reaction of the ferrocyanide of potassium on ferric salts, and whose constitution we have previously indicated.

Soluble ferricyanides do not give any precipitate with ferric salts.

Decomposed by sulphuric acid, the ferricyanide of lead is transformed into sulphate of lead and hydroferricyanic acid $[(\mathrm{Fe^2Cy^{12}})^{\mathrm{VI}}\mathrm{H^6}]$, which latter crystallizes in brownish deliquescent needles.

The iron contained in these different compounds cannot be detected by its usual tests; moreover, they enter into double decomposition with metallic salts, exchanging their metal for hydrogen; they are neutral, and are not poisonous.

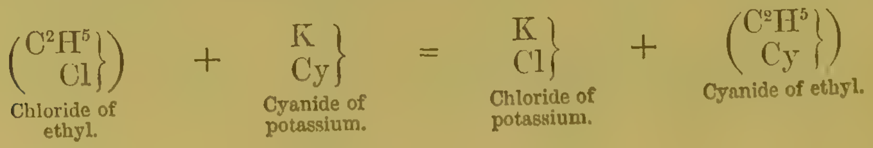
True double cyanides, on the contrary, never have hydrogen substituted for a metal; they are alkaline, poisonous, and the two metals they contain can always be detected. These differences clearly establish that the salts we have just described cannot be regarded as double cyanides.

Cobalt forms compounds, cobalticyanides, which correspond to the ferricyanides; such is the cobalticyanide of potassium $[(\mathrm{Co^2Cy^{12}})^{\mathrm{IV}}\mathrm{K^6}]$. Chromium and manganese give analogous compounds. Nickel, on the contrary, forms compounds which correspond to the ferrocyanides; such is the nickelocyanide of potassium $[(\mathrm{NiCy^6})^{\mathrm{IV}}\mathrm{K^4}]$. Zinc, cadmium, magnesium, etc., do not form any combination of this description; which fact leads us to class nickel with iron and cobalt, and not in the magnesian series.

Platinum gives two orders of cyanogen compounds: platinocyanides $[(\mathrm{PtCy^4})\mathrm{M'^2}]$ and platino-sesquicyanides $[(\mathrm{Pt^2Cy^{10}})\mathrm{M'^4}]$.

Cuprocyanides $[(\mathrm{CuCy^4})\mathrm{M'^2}]$, etc., are furnished by copper.

**Hydrocyanic Ethers.**—When an alcoholic solution of potassic cyanide is acted upon by the hydrochloric or hydrobromic ether of an alcohol, chloride of potassium and a hydrocyanic ether are produced:



$$\underset{\text{Chloride of ethyl.}}{\left(\left.\begin{matrix}\mathrm{C^2H^5}\\\mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\text{Cyanide of potassium.}}{\left.\begin{matrix}\mathrm{K}\\\mathrm{Cy}\end{matrix}\right\}} = \underset{\text{Chloride of potassium.}}{\left.\begin{matrix}\mathrm{K}\\\mathrm{Cl}\end{matrix}\right\}} + \underset{\text{Cyanide of ethyl.}}{\left(\left.\begin{matrix}\mathrm{C^2H^5}\\\mathrm{Cy}\end{matrix}\right\}\right)}$$

This process is general; it succeeds, whatever may be the atomicity of the alcohol whose hydrocyanic ether is to be prepared, and with polyatomic alcohols, whatever may be the degree of etherification to be obtained. By it the hydrocyanic ethers of glycol can be as easily prepared as those of alcohol, and, with the first of these bodies, monocyanhydrin may be as readily obtained as dicyanhydrin.

In order to prepare the hydrocyanic ethers of monatomic alcohols, the alkaline salts of their acid ethers are distilled with cyanide of potassium:

$$\underset{\substack{\text{Ethyl-sulphate}\\ \text{of potassium.}}}{\left(\left.\begin{matrix}SO^{2''}\\ C^2H^5\\ K\end{matrix}\right\} O^2\right)} + \underset{\substack{\text{Cyanide of}\\ \text{potassium.}}}{\left.\begin{matrix}Cy\\ K\end{matrix}\right\}} = \underset{\substack{\text{Cyanide of}\\ \text{ethyl.}}}{\left(\left.\begin{matrix}C^2H^5\\ Cy\end{matrix}\right\}\right)} + \underset{\text{Potassic sulphate.}}{\left(\left.\begin{matrix}SO^{2''}\\ K^2\end{matrix}\right\} O^2\right)}$$

The hydrocyanic ethers of monatomic alcohols, submitted to the influence of hydrating agents, such as a boiling alcoholic solution of potash, absorb two molecules of water and are thereby transformed into ammoniacal salts of acids belonging to series higher by one degree than those to which these ethers belonged; or, rather, the potassic salts of these acids are obtained, ammonia being disengaged:

$$\underset{\substack{\text{Cyanide of}\\ \text{ethyl.}}}{\left(\left.\begin{matrix}C^2H^5\\ CN\end{matrix}\right\}\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\ H\end{matrix}\right\} O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\} O\right)} = \underset{\substack{\text{Propionate of}\\ \text{potassium.}}}{\left(\left.\begin{matrix}C^3H^5O\\ K\end{matrix}\right\} O\right)} + \underset{\text{Ammonia.}}{\left(\left.\begin{matrix}H\\ H\\ H\end{matrix}\right\} N\right)}$$

The hydrocyanic ethers of polyatomic alcohols undergo a similar transformation. They absorb $2(H^2O)$ for each atom of cyanogen radicle they contain. The acids produced belong to series which differ from those to which the ethers employed belong by as many molecules of $CH^2$ as there are molecules of the cyanogen radicle contained in these ethers:

$$\underset{\substack{\text{Cyanhydrin of}\\ \text{glycol.}}}{\left(C^2H^{4''}\left\{\begin{matrix}OH\\ CN\end{matrix}\right.\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\ H\end{matrix}\right\} O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\} O\right)} = \underset{\text{Lactate of potassium.}}{\left(C^2H^{4''}\left\{\begin{matrix}OH\\ CO^2K\end{matrix}\right.\right)}$$

$$+ \underset{\text{Ammonia.}}{(NH^3)}$$

$$\underset{\text{Cyanide of ethylene.}}{\left(C^2H^{4''}\left\{\begin{matrix}CN\\ CN\end{matrix}\right.\right)} + \underset{\text{Potash.}}{2\left(\left.\begin{matrix}K\\ H\end{matrix}\right\} O\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\ H\end{matrix}\right\} O\right)} = \underset{\text{Succinate of potassium.}}{\left(C^2H^{4''}\left\{\begin{matrix}CO^2K\\ CO^2K\end{matrix}\right.\right)}$$

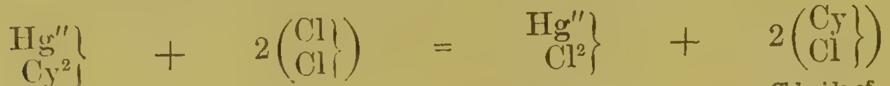
$$+ \underset{\text{Ammonia.}}{2\left(\left.\begin{matrix}H\\ H\\ H\end{matrix}\right\} N\right)}$$

We have already seen (*see* Nitryles) that in the aromatic series the acids obtained by these processes are not the true homologues of those derived by oxidation from the alcohols whose ethers have been employed, and that these latter acids probably correspond to the cyanides of the radicles of phenols. We have also seen that the nitryles, that is to say the hydrocyanic ethers of monatomic phenols or alcohols, fix $H^4$ under the influence of nascent hydrogen, and give compound ammonias belonging to a series one term higher than that of the alcohol or phenol whose radicle they contain.

M. Gauthier has found that the hydrocyanic ethers combine directly with the hydracids of chlorine, bromine, iodine, and sulphur, and even with chloride of boron, forming crystallizable bodies: $(C^2H^5,CN.HCl)$; $(C^2H^5,CN.H^2S)$, etc. The formation of these bodies is explained in the same manner as that of the hydrochlorate of hydrocyanic acid.

The same chemist has discovered a very remarkable case of isomerism. The cyanide of ethyl prepared by the action of the cyanide of silver on the iodide of ethyl, is not identical with that resulting from the action of cyanide of potassium on potassic sulphovinate. The first is volatile at 82°, has a very disagreeable odour, and when cold combines instantaneously with hydrochloric acid, developing heat like ammonia. The second boils at 98°, has an ethereal odour which is not disagreeable when the salt is pure, and requires some time in order to unite with the hydracids. These differences between these two isomers may perhaps be explained by representing ordinary cyanide of ethyl by the formula $[(CH)'''.N]$ and M. Gauthier's cyanide by the formula $\left(\left.\begin{matrix}C''\\H\end{matrix}\right\}N\right)$.[*]

**Chlorides of Cyanogen.**—If moist mercuric cyanide be left in a flask full of chlorine, gaseous chloride of cyanogen $\left.\begin{matrix}Cy\\Cl\end{matrix}\right\}$ is produced:

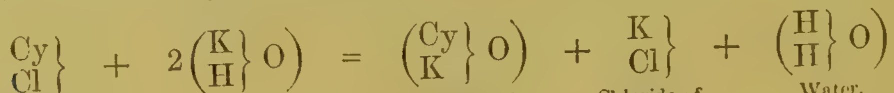


$$\left.\begin{matrix}Hg''\\Cy^2\end{matrix}\right\} + 2\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}\right) = \left.\begin{matrix}Hg''\\Cl^2\end{matrix}\right\} + 2\left(\left.\begin{matrix}Cy\\Cl\end{matrix}\right\}\right)$$

Mercuric cyanide. Chlorine. Mercuric chloride. Chloride of cyanogen.

Gaseous chloride of cyanogen is solidified by a cold of −18°, melts at −15°, and begins to boil at −12°, under the ordinary pressure of the atmosphere; water dissolves 25 times, ether 50 times, and alcohol 100 times its volume. When left in a hermetically-sealed tube, gaseous chloride of cyanogen is slowly converted into solid chloride.

The alkalies transform chloride of cyanogen into alkaline chloride and cyanate, or, rather, into chloride, carbonic anhydride, and ammonia; these two latter bodies being produced secondarily by the action of the alkali on the cyanate formed:



$$\left.\begin{matrix}Cy\\Cl\end{matrix}\right\} + 2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}Cy\\K\end{matrix}\right\}O\right) + \left.\begin{matrix}K\\Cl\end{matrix}\right\} + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

Chloride of cyanogen. Potash. Cyanate of potassium. Chloride of potassium. Water.

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[*] From a private communication.

On transmitting a current of chlorine into concentrated hydrocyanic acid cooled to 0°, at a certain time a lighter layer will be seen to separate from the remainder of the liquid; this layer is a combination of chloride of cyanogen and hydrocyanic acid, and when washed with iced water and dried, its formula is $[(CyCl)^2HCy]$, and it boils at 20°. If it be mixed with mercuric oxide in a cold vessel, and then distilled, transmitting the vapours over chloride of calcium, a liquid is obtained which is not inflammable, is volatile at 15°, and solidified at $-5°$ or $-6°$, and the formula of which is $(CyCl)$. This is a liquid modification of the chloride of cyanogen. It was formerly believed that this body corresponded to the double formula $(Cy^2Cl^2)$; but its vapour density, recently determined, proves that, like the gaseous chloride, it corresponds to the simple formula $\left.\begin{matrix}Cy\\Cl\end{matrix}\right\}$. Liquid chloride of cyanogen, when pure, may be preserved for any length of time; but if it be prepared by transmitting chlorine into dilute hydrocyanic acid and simply distilling, without washing with iced water or treating by mercuric oxide, the product obtained is soon transformed into solid chloride of cyanogen.

The solid chloride $\left.\begin{matrix}Cy^3\\Cl^3\end{matrix}\right\}$ is obtained by the action in sunlight of chlorine in excess on anhydrous hydrocyanic acid. This body forms brilliant needles of a density of 1·32; it melts at 140° and boils at 190°. It is only sparingly soluble in water, but the solution is very poisonous; it is very soluble in alcohol and in ether. Its alcoholic solution is quickly transformed into hydrochloric and cyanuric acids:

$$\underset{\text{Solid chloride of cyanogen.}}{\left.\begin{matrix}Cy^3\\Cl^3\end{matrix}\right\}} + \underset{\text{Water.}}{3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Cyanuric acid.}}{\left(\left.\begin{matrix}Cy^3\\H^3\end{matrix}\right\}O^3\right)} + \underset{\text{Hydrochloric acid.}}{3\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)}$$

This transformation is instantaneous if an alkali be present.

Some chemists still doubt the existence of gaseous chloride of cyanogen, and think that it is merely the vapour of more or less impure liquid chloride. This subject requires further research.

**Bromide and Iodide of Cyanogen** $\left.\begin{matrix}Cy\\Br\end{matrix}\right\}$ and $\left.\begin{matrix}Cy\\I\end{matrix}\right\}$.— These bodies are obtained by submitting mercuric cyanide to the action of bromine or iodine. The equations which represent their formation are identical with that given to explain the production of a simple chloride, substituting bromine or iodine for chlorine.

The chemical properties of the iodide and bromide of cyanogen are similar to those of the chloride (CyCl). Condensed bromides and iodides are unknown.

Bromide of cyanogen is solid; it melts at +4°, according to some, but requires a higher temperature according to others. This would appear to indicate the existence of different bromides which have been confounded with each other.

The iodide is volatilized without residue at +45°.

**Cyanic Acid** $\left(\left.\begin{matrix}Cy\\H\end{matrix}\right\}O\right)$.—Potassic cyanate is obtained by heating dried ferrocyanide of potassium mixed with peroxide of manganese on an iron plate, and treating with boiling alcohol. The filtered liquid deposits potassic cyanate on cooling. In this reaction the ferrocyanide is first transformed, under the influence of heat, into potassic cyanide and carbide of iron, and the potassic cyanide is then oxidized at the cost of the peroxide of manganese:

$$\underset{\text{Cyanide of potassium.}}{2\left(\left.\begin{matrix}K\\Cy\end{matrix}\right\}\right)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} = \underset{\text{Cyanate of potassium.}}{2\left(\left.\begin{matrix}Cy\\K\end{matrix}\right\}O\right)}$$

Cyanic acid cannot be extracted from the cyanates; but this acid is obtained by distilling cyanuric acid in a small retort:

$$\underset{\text{Cyanuric acid.}}{\left(\left.\begin{matrix}Cy^3\\H^3\end{matrix}\right\}O^3\right)} = \underset{\text{Cyanic acid.}}{3\left(\left.\begin{matrix}Cy\\H\end{matrix}\right\}O\right)}$$

When left to itself, cyanic acid is converted into a solid white mass called cyamelid: this transformation is accompanied by a disengagement of heat. Cyamelid is retransformed into cyanic acid by distillation.

The alkalies transform cyanic acid into cyanates; if these salts be heated with an excess of base, they are decomposed into alkaline carbonate and ammonia:

$$\underset{\text{Potassic cyanate.}}{\left(\left.\begin{matrix}CN\\K\end{matrix}\right\}O\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic carbonate.}}{\left(\left.\begin{matrix}CO''\\K^2\end{matrix}\right\}O^2\right)} + \underset{\text{Ammonia.}}{(NH^3)}$$

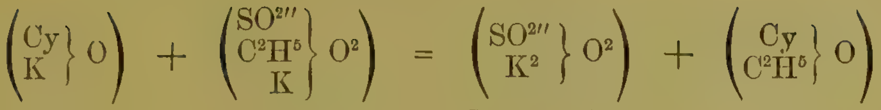
Under the influence of water, cyanic acid undergoes an analogous decomposition:

$$\underset{\text{Cyanic acid.}}{\left(\left.\begin{matrix}CN\\H\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Carbonic anhydride.}}{(CO^2)} + \underset{\text{Ammonia.}}{(NH^3)}$$

Urea is also produced in this case, in consequence of the secondary action exercised by the ammonia formed, on some cyanic acid remaining undecomposed.

The action of cyanic acid on the alcohols give rise, not to the formation of cyanic ethers, but to that of ethers of an acid whose formula is $(C^2H^4N^2O^3)$, and which is called allophanic acid.

Cyanic ethers are obtained by distilling the alkaline salt of an acid ether with potassic cyanate:

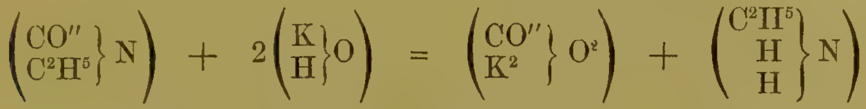


$$\left(\left.\begin{matrix}\mathrm{Cy}\\ \mathrm{K}\end{matrix}\right\}\mathrm{O}\right) + \left(\left.\begin{matrix}\mathrm{SO}^{2\prime\prime}\\ \mathrm{C}^2\mathrm{H}^5\\ \mathrm{K}\end{matrix}\right\}\mathrm{O}^2\right) = \left(\left.\begin{matrix}\mathrm{SO}^{2\prime\prime}\\ \mathrm{K}^2\end{matrix}\right\}\mathrm{O}^2\right) + \left(\left.\begin{matrix}\mathrm{Cy}\\ \mathrm{C}^2\mathrm{H}^5\end{matrix}\right\}\mathrm{O}\right)$$

Potassic cyanate. Potassic ethyl-sulphate. Potassic sulphate. Cyanate of ethyl.

M. Gal has shown that cyanic, like hydrocyanic ethers, are capable of uniting with hydracids.

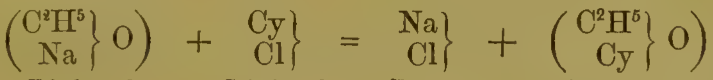
Under the influence of alkalies, the cyanic ethers undergo a decomposition analogous to that which cyanic acid undergoes; but as the typical hydrogen of this acid is here replaced by a radicle of alcohol, the ammonia which is formed contains an alcohol radicle substituted for an atom of hydrogen:



$$\left(\left.\begin{matrix}\mathrm{CO}''\\ \mathrm{C}^2\mathrm{H}^5\end{matrix}\right\}\mathrm{N}\right) + 2\left(\left.\begin{matrix}\mathrm{K}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right) = \left(\left.\begin{matrix}\mathrm{CO}''\\ \mathrm{K}^2\end{matrix}\right\}\mathrm{O}^2\right) + \left(\left.\begin{matrix}\mathrm{C}^2\mathrm{H}^5\\ \mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{N}\right)$$

Cyanate of ethyl. Potash. Potassic carbonate. Ethylamine.

**Cyanetholine.**—This body is an isomer of cyanate of ethyl, and has been obtained by M. Cloez by causing chloride of cyanogen to act on the ethylate of sodium:



$$\left(\left.\begin{matrix}\mathrm{C}^2\mathrm{H}^5\\ \mathrm{Na}\end{matrix}\right\}\mathrm{O}\right) + \left.\begin{matrix}\mathrm{Cy}\\ \mathrm{Cl}\end{matrix}\right\} = \left.\begin{matrix}\mathrm{Na}\\ \mathrm{Cl}\end{matrix}\right\} + \left(\left.\begin{matrix}\mathrm{C}^2\mathrm{H}^5\\ \mathrm{Cy}\end{matrix}\right\}\mathrm{O}\right)$$

Ethylate of sodium. Chloride of cyanogen. Chloride of sodium. Cyanetholine.

Instead of being decomposed by potash into ethylamine and potassic carbonate, as is the case with the cyanate of ethyl of M. Wurtz, cyanetholine, like ethers in general, splits up into alcohol and cyanic acid, or rather, into alcohol, and the products of the decomposition of cyanic acid by the alkalies, *i.e.*, ammonia and carbonic anhydride.

The hydracids do not unite with cyanetholine, but they transform it into chloride or bromide of ethyl, and cyanuric acid resulting from the condensation of cyanic acid.

From these facts it follows that the names applied to cyanic acid and its ethers ought to be changed. Cyanetholine is the true cyanic ether containing the radicle CN united to ethyl by means of O; the cyanic ethers of M. Wurtz are the alcoholic derivatives of carbimide $\left(\left.\begin{matrix}\mathrm{CO}''\\ \mathrm{H}\end{matrix}\right\}\mathrm{N}\right)$.

Their constitution and that of cyanetholine is expressed by the following figures:

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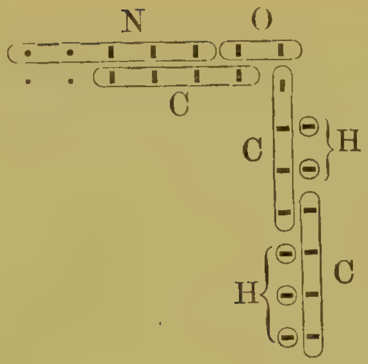
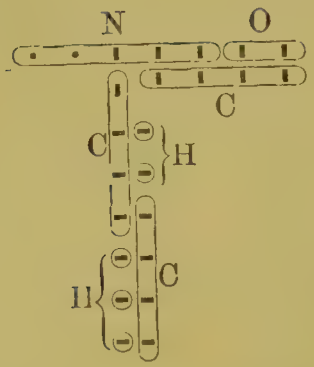


$$=\left(\left.\begin{matrix}\mathrm{NC}\\ \mathrm{C^2H^5}\end{matrix}\right\}\mathrm{O}\right)$$ Cyanetholine.



$$=\left(\left.\begin{matrix}\mathrm{CO''}\\ \mathrm{C^2H^5}\end{matrix}\right\}\mathrm{N}\right)$$ Cyanic ether (ethyl-carbimide).

It is probable that similar isomers exist, and that, seeing the facility with which cyanogenized bodies are transformed, compounds which do not contain the cyanogen radicle are improperly called cyanogen compounds. This name should be reserved exclusively for bodies containing nitrogen saturated in three of its atomicities by carbon, the fourth unoccupied atomicity of the carbon uniting with the various residues. Those bodies in which only two atomicities of nitrogen are saturated by carbon, the third being united to a radicle, while the two free atomicities of the carbon are united to oxygen or remain free, are not cyanogen compounds, but *carbonic imides* or analogous bodies.

**Cyanuric Acid** $\left(\left.\begin{matrix}\mathrm{Cy^3}\\ \mathrm{H^3}\end{matrix}\right\}\mathrm{O^3}\right)$.—The best method of obtaining this body consists, according to M. Wurtz, in submitting urea in a state of fusion to the action of a current of dry chlorine:

$$\underset{\text{Urea.}}{3(\mathrm{CH^4N^2O})} + \underset{\text{Chlorine.}}{3\left(\left.\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right\}\right)} = \underset{\text{Cyanuric acid.}}{\left(\left.\begin{matrix}\mathrm{(CO'')^3}\\ \mathrm{H^3}\end{matrix}\right\}\mathrm{N^3}\right)} + \underset{\text{Hydrochloric acid.}}{5\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{Cl}\end{matrix}\right\}\right)}$$

$$+ \underset{\text{Chloride of ammonium.}}{\left(\left.\begin{matrix}\mathrm{NH^4}\\ \mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\text{Nitrogen.}}{\left.\begin{matrix}\mathrm{N}\\ \mathrm{N}\end{matrix}\right\}}$$

The chloride of ammonium is removed by solution in cold water, and the cyanuric acid is then dissolved in boiling water and crystallized.

Under the influence of hydrating agents, cyanuric, like cyanic acid, is converted into carbonic anhydride and ammonia.

Cyanuric ethers are obtained in the same manner as cyanic ethers, that is to say, by the action of acid ethers on cyanurates. Alkalies decompose them, producing an alkaline carbonate and a compound ammonia. The reaction is the same as with cyanic ethers, but cyanuric acid furnishes three molecules of each of these products of decomposition, where cyanic acid only furnishes one.

**Dicyanic Acid.**—Intermediate between cyanic acid $\left(\left.\begin{matrix}\mathrm{Cy}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)$ and cyanuric acid $\left(\left.\begin{matrix}\mathrm{Cy}^3\\\mathrm{H}^3\end{matrix}\right\}\mathrm{O}^3\right)$, it is natural to anticipate the existence of another acid, $\left(\left.\begin{matrix}\mathrm{Cy}^2\\\mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right)$ dicyanic acid. M. Poensgen has recently found this hypothesis to be correct.

To obtain this acid, urea is heated to 140° with the iodide of cyanogen; cyanurea is thus produced:

$$\underset{\text{Urea.}}{(\mathrm{CH^4N^2O})} + \underset{\text{Iodide of cyanogen.}}{\left(\left.\begin{matrix}\mathrm{CN}\\\mathrm{I}\end{matrix}\right\}\right)} = \underset{\text{Cyanurea.}}{(\mathrm{CH^3(CN)N^2O})} + \underset{\text{Hydriodic acid.}}{\left.\begin{matrix}\mathrm{H}\\\mathrm{I}\end{matrix}\right\}}$$

Cyanurea being then submitted to the action of nitrous acid, is transformed into water, nitrogen, and dicyanic acid:

$$\underset{\text{Cyanurea.}}{(\mathrm{CH^3(CN)N^2O})} + \underset{\text{Nitrous acid.}}{\left(\left.\begin{matrix}\mathrm{NO}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + \underset{\text{Nitrogen.}}{\left.\begin{matrix}\mathrm{N}\\\mathrm{N}\end{matrix}\right\}} + \underset{\text{Dicyanic acid.}}{\left(\left.\begin{matrix}(\mathrm{CN})^2\\\mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2\right)}$$

Dicyanic acid is bibasic, and has a great tendency to form acid salts; under the influence of hydrating agents it is decomposed, giving two molecules of carbonic anhydride and two molecules of ammonia; it therefore undergoes a transformation precisely analogous to those of cyanic and cyanuric acids.

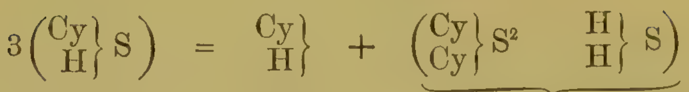
**Sulphocyanic Acid** (*improperly called Hydrosulphocyanic Acid*) $\left(\left.\begin{matrix}\mathrm{Cy}\\\mathrm{H}\end{matrix}\right\}\mathrm{S}\right)$.—Alkaline sulphocyanates are obtained by heating a cyanide with sulphur:

$$\underset{\text{Cyanide of potassium.}}{2\left(\left.\begin{matrix}\mathrm{K}\\\mathrm{Cy}\end{matrix}\right\}\right)} + \underset{\text{Sulphur.}}{\left.\begin{matrix}\mathrm{S}\\\mathrm{S}\end{matrix}\right\}} = \underset{\text{Sulphocyanate of potassium.}}{2\left(\left.\begin{matrix}\mathrm{Cy}\\\mathrm{K}\end{matrix}\right\}\mathrm{S}\right)}$$

From the alkaline sulphocyanates, those of metals may be prepared by double decomposition, and by decomposing the sulphocyanate of mercury by sulphuretted hydrogen sulphocyanic acid is obtained.

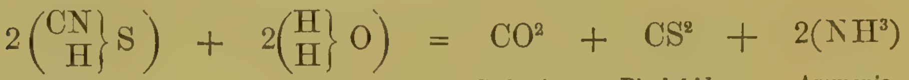
This acid and its salts colour ferric salts blood-red, in consequence of the formation of ferric sulphocyanate.

Sulphocyanic acid is very instable, even when diluted, When dry it is still more instable, and decomposes into hydrocyanic and persulphohydrocyanic acids:



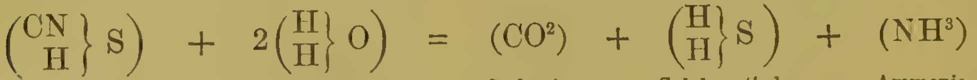
$$\underset{\text{Sulphocyanic acid.}}{3\left(\left.\begin{matrix}\mathrm{Cy}\\\mathrm{H}\end{matrix}\right\}\mathrm{S}\right)} = \underset{\text{Hydrocyanic acid.}}{\left.\begin{matrix}\mathrm{Cy}\\\mathrm{H}\end{matrix}\right\}} + \underbrace{\left(\left.\begin{matrix}\mathrm{Cy}\\\mathrm{Cy}\end{matrix}\right\}\mathrm{S}^2 \quad \left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{S}\right)}_{\text{Persulphohydrocyanic acid.}}$$

When moist, it is transformed sometimes into carbonic anhydride, bisulphide of carbon and ammonia :



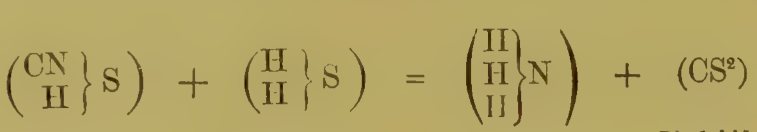
$$\underset{\text{Sulphocyanic acid.}}{2\left(\left.\begin{matrix}\mathrm{CN}\\\mathrm{H}\end{matrix}\right\}\mathrm{S}\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\text{Carbonic anhydride.}}{\mathrm{CO}^2} + \underset{\text{Bisulphide of carbon.}}{\mathrm{CS}^2} + \underset{\text{Ammonia.}}{2(\mathrm{NH}^3)}$$

sometimes into carbonic anhydride, sulphuretted hydrogen and ammonia :



$$\underset{\text{Sulphocyanic acid.}}{\left(\left.\begin{matrix}\mathrm{CN}\\\mathrm{H}\end{matrix}\right\}\mathrm{S}\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\text{Carbonic anhydride.}}{(\mathrm{CO}^2)} + \underset{\text{Sulphuretted hydrogen.}}{\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{S}\right)} + \underset{\text{Ammonia.}}{(\mathrm{NH}^3)}$$

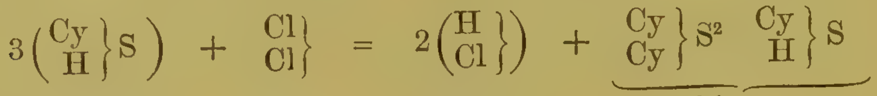
Under the prolonged influence of sulphuretted hydrogen, it gives ammonia and bisulphide of carbon :



$$\underset{\text{Sulphocyanic acid.}}{\left(\left.\begin{matrix}\mathrm{CN}\\\mathrm{H}\end{matrix}\right\}\mathrm{S}\right)} + \underset{\text{Sulphuretted hydrogen.}}{\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{S}\right)} = \underset{\text{Ammonia.}}{\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{N}\right)} + \underset{\text{Bisulphide of carbon.}}{(\mathrm{CS}^2)}$$

This reaction is analogous to that produced when water acts on cyanic acid.

Chlorine and nitric acid cause a yellow precipitate of persulphocyanogen in sulphocyanic acid, and in solutions of the sulphocyanates :



$$\underset{\text{Sulphocyanic acid.}}{3\left(\left.\begin{matrix}\mathrm{Cy}\\\mathrm{H}\end{matrix}\right\}\mathrm{S}\right)} + \underset{\text{Chlorine.}}{\left.\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right\}} = \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{Cl}\end{matrix}\right\}\right)} + \underbrace{\left.\begin{matrix}\mathrm{Cy}\\\mathrm{Cy}\end{matrix}\right\}\mathrm{S}^2 \quad \left.\begin{matrix}\mathrm{Cy}\\\mathrm{H}\end{matrix}\right\}\mathrm{S}}_{\text{Persulphocyanogen.}}$$

**Seleniocyanic Acid.**—Potassic seleniocyanate is obtained by calcining the potassic cyanide with selenium. The solution of this salt, when added to that of a salt of lead, gives a precipitate of seleniocyanate of lead, which, when treated by sulphuretted hydrogen, furnishes seleniocyanic acid. This acid is very instable, and the products of decomposition to which it gives rise are imperfectly known.

**Cyanic Amides.**—Cyanamide $\left(\left.\begin{matrix}\mathrm{Cy}\\\mathrm{H}^2\end{matrix}\right\}\mathrm{N}\right)$ is prepared by the action of gaseous chloride of cyanogen on ammonia in ethereal solution : chloride of ammonium is deposited, cyanamide remains dissolved, and is obtained by evaporating the ether in a water-bath.

$$\underset{\text{Chloride of cyanogen.}}{\left.\begin{matrix}Cy\\Cl\end{matrix}\right\}} + \underset{\text{Ammonia.}}{2\left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right)} = \underset{\text{Chloride of ammonium.}}{\left(\left.\begin{matrix}NH^4\\Cl\end{matrix}\right\}\right)} + \underset{\text{Cyanamide.}}{\left(\left.\begin{matrix}Cy\\H\\H\end{matrix}\right\}N\right)}$$

Under the influence of alkalies, cyanamide furnishes ammonia and the products of the decomposition of cyanates (carbonic anhydride and ammonia). If it be heated to 150°, it is transformed into a polymeric alkali, melamine $\left(\left.\begin{matrix}Cy^3\\H^3\\H^3\end{matrix}\right\}N^3\right)$, which is also produced when melam, a neutral body with which it is isomeric, is submitted to the action of boiling potash. Melam itself remains as residue when the sulphocyanate of ammonium is decomposed by heat.

When melamine is boiled for some time with an alkaline solution, it disengages ammonia, and is successively transformed into ammeline, ammelid, and cyanuric acid:

$$\underset{\text{Melam and melamine.}}{\left((CN)^3\left\{\begin{matrix}NH^2\\NH^2\\NH^2\end{matrix}\right.\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Ammonia.}}{\left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right)} + \underset{\text{Ammeline.}}{\left((CN)^3\left\{\begin{matrix}NH^2\\NH^2\\OH\end{matrix}\right.\right)}$$

$$\underset{\text{Ammeline.}}{\left((CN)^3\left\{\begin{matrix}NH^2\\NH^2\\OH\end{matrix}\right.\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Ammonia.}}{\left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right)} + \underset{\text{Ammelid.}}{\left((CN)^3\left\{\begin{matrix}NH^2\\OH\\OH\end{matrix}\right.\right)}$$

$$\underset{\text{Ammelid.}}{\left((CN^3)\left\{\begin{matrix}NH^2\\OH\\OH\end{matrix}\right.\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Ammonia.}}{\left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right)} + \underset{\text{Cyanuric acid.}}{\left((CN)^3\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.\right)}$$

A sulphuretted ammelid $\left((CN)^3\left\{\begin{matrix}NH^2\\SH\\SH\end{matrix}\right.\right)$ is obtained by a very complicated reaction, when persulphocyanogen is dissolved in hydrosulphate of potassium; this body is called sulphomellonic acid.

When ammonia acts on the solid chloride of cyanogen, a body is obtained representing melamine, of which one of the $NH^2$ groups is replaced by Cl. It is chlorocyanamide $\left(Cy^3\left\{\begin{matrix}NH^2\\NH^2\\Cl\end{matrix}\right.\right)$.

$$\underset{\text{Chloride of cyanogen.}}{\left.\begin{matrix}Cy^3\\Cl^3\end{matrix}\right\}} + \underset{\text{Ammonia.}}{4\left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right)} = \underset{\text{Chloride of ammonium.}}{2\left(\left.\begin{matrix}NH^4\\Cl\end{matrix}\right\}\right)} + \underset{\text{Chlorocyanamide.}}{\left((Cy)^3\left\{\begin{matrix}NH^2\\NH^2\\Cl\end{matrix}\right.\right)}$$

Dicyanamide ($NCy^2H$) is unknown; but, by the action of a powerful heat, many of the cyanic compounds give a yellow residue which is formed by the condensation of three molecules of dicyanamide into one. It is hydromellon $\left(\left.\begin{matrix}Cy^3\\Cy^3\\H^3\end{matrix}\right\}N^3\right)$. Liebig, who discovered this body, believing it to be free from hydrogen, represented it by the formula $(C^3N^4) = n(NCy^3)$, and called it mellon; but Gerhardt, Laurent, and Wœlkel, have clearly shown that this body contains hydrogen, and has the formula $\left(\left.\begin{matrix}Cy^3\\Cy^3\\H^3\end{matrix}\right\}N^3\right)$.

When heated with potassium, hydromellon exchanges $H^2$ for $K^2$, and gives potassic mellonide $\left(\left.\begin{matrix}Cy^3\\Cy^3\\K^2\\H\end{matrix}\right\}N^3\right)$. Boiling concentrated potash transforms hydromellon into potassic cyamellurate and ammonia.

Chemists are not quite agreed as to the reaction which takes place, nor as to the formula of cyamelluric acid, which is $(C^6H^3N^7O^3)$ according to Liebig, and $(C^6H^4N^8O^2)$ according to Gerhardt.

**Tricyanamide** $NCy^3$ has not as yet been obtained, and no polymer of this body is known.

**Constitution of Cyanogen Compounds.**—So far we have admitted that all the bodies just studied contain the cyanogen radicle, that is to say, an atom of carbon, three atomicities of which are saturated by nitrogen.

However, such formulæ do not appear applicable to all these compounds. The discovery of cyanetholine by M. Cloez proves that among these bodies there are isomers which must be represented by distinct rational formulæ.

Hydrocyanic acid and ethers appear really to contain the cyanogen radicle. If such be the case, the hydrogen and the radicles of alcohol are directly united to the carbon, and the transformations these bodies undergo under the influence of hydrating agents are easily explained:

$$\underbrace{\left(\left.\begin{matrix}CN\\C^2H^5\end{matrix}\right\}\right) = (C^3H^{5'''}N)}_{\text{Cyanide of ethyl.}} + \underbrace{2(H^2O)}_{\text{Water.}} = \underbrace{(NH^3)}_{\text{Ammonia.}} + \underbrace{(C^3H^5O.OH)}_{\text{Propionic acid.}}$$

The cyanetholine of M. Cloez also appears to contain cyanogen united to oxethyl, which explains clearly its decomposition by bases into alcohol and metallic cyanate. The cyanic ethers of M. Wurtz, on the contrary, do not appear to belong to the cyanogen series; they are rather compound carbonic imides $\left(\left.\begin{matrix}CO''\\R'\end{matrix}\right\}N\right)$; that is to say, the radicle $R'$ is not united, directly, either to the carbon or to the oxygen, but to the nitrogen, which is only attached to the carbon by two atomicities, the other two atomicities of the carbon being saturated by oxygen. It is almost impossible at present to decide what is the constitution of sulphocyanic acid, cyanic amides, and their condensed derivatives: as this is doubtful, it is better to retain the formulæ in which cyanogen is admitted; these formulæ are very simple, and account for most of their reactions.

Whatever may be the formulæ adopted, the property all these bodies possess of being condensed is readily explained: if they contain cyanogen, that is to say, a triatomic and monovalent radicle, two atomicities of this radicle remain, by which it can unite with itself; if they are carbonic imides, they contain the biatomic radicle $\mathrm{CO''}$, which, like all polyatomic radicles, possesses the property of accumulating in molecules.

In the following table, we will place side by side the rational formulæ of the known cyanogen compounds, considered as containing cyanogen or as being carbonic amides. But it is important to remark that those formulæ which belong to possible bodies, indicate isomerisms, and cannot be considered as different methods of explaining the composition of the same bodies.

Among these possible isomerisms, only one is known with certainty; it is that of the cyanetholine of M. Cloez and the cyanate of ethyl of M. Wurtz.

| FORMULÆ IN WHICH THE CYANOGEN RADICLE Cy = CN IS ADMITTED. | FORMULÆ IN WHICH THE CYANOGEN RADICLE IS NOT ADMITTED. |
|---|---|
| $\left.\begin{matrix}\mathrm{Cy}\\ \mathrm{Cy}\end{matrix}\right\} = \left.\begin{matrix}\mathrm{CN}\\ \mathrm{CN}\end{matrix}\right\}$<br>Free cyanogen. | $\mathrm{C^{2\mathrm{VI}}}\Big\}\mathrm{N^2}$<br>Cyanogen. |
| $\left.\begin{matrix}\mathrm{Cy}^{n}\\ \mathrm{Cy}^{n}\end{matrix}\right\} = \left.\begin{matrix}\mathrm{CN}^{n}\\ \mathrm{CN}^{n}\end{matrix}\right\}$<br>Paracyanogen. | $\left(\mathrm{C^{2\mathrm{VI}}}\Big\}\mathrm{N^2}\right)^{n}$<br>Paracyanogen. |
| $\left.\begin{matrix}\mathrm{Cy}\\ \mathrm{H}\end{matrix}\right\} = \left.\begin{matrix}\mathrm{CN}\\ \mathrm{H}\end{matrix}\right\}$<br>Hydrocyanic acid. | $\left.\begin{matrix}\mathrm{C''}\\ \mathrm{H}\end{matrix}\right\}\mathrm{N}$<br>Hydrocyanic acid. |
| $\left.\begin{matrix}\mathrm{Cy}\\ \mathrm{M'}\end{matrix}\right\} = \left.\begin{matrix}\mathrm{CN}\\ \mathrm{M'}\end{matrix}\right\}$<br>Simple cyanides. | $\left.\begin{matrix}\mathrm{C''}\\ \mathrm{M'}\end{matrix}\right\}\mathrm{N}$<br>Simple cyanides. |
| $\left.\begin{matrix}\mathrm{Cy}^{n}\\ \mathrm{M}^{n}\end{matrix}\right\} = \left.\begin{matrix}\mathrm{CN}^{n}\\ \mathrm{M}^{n}\end{matrix}\right\}$<br>Cyanides of polyatomic radicles. | $\left.\begin{matrix}\mathrm{C}''^{n}\\ \mathrm{M}^{n}\end{matrix}\right\}\mathrm{N}$<br>Cyanides of polyatomic radicles. |
| $\begin{matrix}\left.\begin{matrix}\mathrm{C^2H^4}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\\ \mathrm{Cy}\end{matrix} = \begin{matrix}\left.\begin{matrix}\mathrm{C^2H^4}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\\ \mathrm{CN}\end{matrix}$<br>Cyanhydrins. | $\left.\begin{matrix}\left(\left.\begin{matrix}\mathrm{C^2H^{4''}}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)'\\ \mathrm{C''}\end{matrix}\right\}\mathrm{N}$<br>Cyanhydrins. |
| $\left.\begin{matrix}(\mathrm{FeCy^6})^{\mathrm{IV}}\\ \mathrm{M'^4}\end{matrix}\right\} = \left.\begin{matrix}(\mathrm{Fe[CN]^6})^{\mathrm{IV}}\\ \mathrm{M'^4}\end{matrix}\right\}$<br>Ferrocyanides. | $\left.\begin{matrix}\mathrm{C''^2Fe''}\\ \mathrm{C''^2M'^2}\\ \mathrm{C''^2M'^2}\end{matrix}\right\}\mathrm{N^6}$<br>Ferrocyanides. |

$$\left.\begin{array}{r}(\mathrm{Fe}^2\mathrm{Cy}^{12})^{\mathrm{vi}}\\ \mathrm{M}'^6\end{array}\right\} = \left.\begin{array}{r}(\mathrm{Fe}^2[\mathrm{CN}]^{12})^{\mathrm{vi}}\\ \mathrm{M}'^6\end{array}\right\}$$

Ferricyanides.

$$\left.\begin{array}{r}\mathrm{Cy}\\ \mathrm{Cl}\end{array}\right\} = \left.\begin{array}{r}\mathrm{CN}\\ \mathrm{Cl}\end{array}\right\}$$

Gaseous and liquid chloride of cyanogen.

$$\left.\begin{array}{r}\mathrm{Cy}^3\\ \mathrm{Cl}^3\end{array}\right\} = \left.\begin{array}{r}(\mathrm{CN})^3\\ \mathrm{Cl}^3\end{array}\right\}$$

Solid chloride of cyanogen.

$$\left.\begin{array}{r}\mathrm{Cy}\\ \mathrm{Br}\end{array}\right\} = \left.\begin{array}{r}\mathrm{CN}\\ \mathrm{Br}\end{array}\right\}$$

Bromide of cyanogen.

$$\left.\begin{array}{r}\mathrm{Cy}\\ \mathrm{I}\end{array}\right\} = \left.\begin{array}{r}\mathrm{CN}\\ \mathrm{I}\end{array}\right\}$$

Iodide of cyanogen.

$$\left.\begin{array}{r}\mathrm{Cy}\\ \mathrm{H}\end{array}\right\}\mathrm{O} = \left.\begin{array}{r}\mathrm{CN}\\ \mathrm{H}\end{array}\right\}\mathrm{O}$$

Cyanic acid.

$$\left.\begin{array}{r}\mathrm{Cy}^2\\ \mathrm{H}^2\end{array}\right\}\mathrm{O}^2 = \left.\begin{array}{r}(\mathrm{CN})^2\\ \mathrm{H}^2\end{array}\right\}\mathrm{O}^2$$

Dicyanic acid.

$$\left.\begin{array}{r}\mathrm{Cy}^3\\ \mathrm{H}^3\end{array}\right\}\mathrm{O}^3 = \left.\begin{array}{r}(\mathrm{CN})^3\\ \mathrm{H}^3\end{array}\right\}\mathrm{O}^3$$

Cyanuric acid.

$$\left.\begin{array}{r}\mathrm{Cy}\\ \mathrm{C}^2\mathrm{H}^5\end{array}\right\}\mathrm{O} = \left.\begin{array}{r}\mathrm{CN}\\ \mathrm{C}^2\mathrm{H}^5\end{array}\right\}\mathrm{O}$$

Cyanate of ethyl of M. Cloez (cyanetholine).

$$\left.\begin{array}{r}\mathrm{Cy}\\ \mathrm{H}\\ \mathrm{H}\end{array}\right\}\mathrm{N} = \left.\begin{array}{r}\mathrm{CN}\\ \mathrm{H}\\ \mathrm{H}\end{array}\right\}\mathrm{N}$$

Cyanamide.

$$\mathrm{Cy}^3\left\{\begin{array}{l}\mathrm{NH}^2\\ \mathrm{NH}^2\\ \mathrm{NH}^2\end{array}\right. = (\mathrm{CN})^3\left\{\begin{array}{l}\mathrm{NH}^2\\ \mathrm{NH}^2\\ \mathrm{NH}^2\end{array}\right.$$

Melamine.

$$\mathrm{Cy}^3\left\{\begin{array}{l}\mathrm{NH}^2\\ \mathrm{NH}^2\\ \mathrm{OH}\end{array}\right. = (\mathrm{CN})^3\left\{\begin{array}{l}\mathrm{NH}^2\\ \mathrm{NH}^2\\ \mathrm{OH}\end{array}\right.$$

Ammeline.

$$\left.\begin{array}{l}\left.\begin{array}{l}\mathrm{C}''^4\mathrm{M}'^2\\ \mathrm{C}''^4\mathrm{M}'^2\\ \mathrm{C}''^4\mathrm{M}'^2\end{array}\right\}\mathrm{Fe}^{2\mathrm{vi}}\end{array}\right\}\mathrm{N}^{12}$$

Ferricyanides.

$$\left.\begin{array}{r}\mathrm{C}''\\ \mathrm{Cl}\end{array}\right\}\mathrm{N}$$

Gaseous and liquid chloride of cyanogen.

$$\left.\begin{array}{r}\mathrm{C}''^3\\ \mathrm{Cl}^3\end{array}\right\}\mathrm{N}^3$$

Solid chloride of cyanogen.

$$\left.\begin{array}{r}\mathrm{C}''\\ \mathrm{Br}\end{array}\right\}\mathrm{N}$$

Bromide of cyanogen.

$$\left.\begin{array}{r}\mathrm{C}''\\ \mathrm{I}\end{array}\right\}\mathrm{N}$$

Iodide of cyanogen.

$$\left.\begin{array}{c}\mathrm{CO}''\\ \mathrm{H}\end{array}\right\}\mathrm{N}$$

Cyanic acid (carbimide).

$$\left.\begin{array}{l}\mathrm{CO}''\\ \mathrm{CO}''\\ \mathrm{H}^2\end{array}\right\}\mathrm{N}^2$$

Dicyanic acid (dicarbo-diamide).

$$\left.\begin{array}{l}\mathrm{CO}''\\ \mathrm{CO}''\\ \mathrm{CO}''\\ \mathrm{H}^3\end{array}\right\}\mathrm{N}^3$$

Cyanuric acid (tricarbo-triamide).

$$\left.\begin{array}{l}\mathrm{CO}''\\ \mathrm{C}^2\mathrm{H}^5\end{array}\right\}\mathrm{N}$$

Cyanate of ethyl of M. Wurtz (ethyl-carbimide).

$$\left.\begin{array}{l}\mathrm{C}^{\mathrm{IV}}\\ \mathrm{H}^2\end{array}\right\}\mathrm{N}^2$$

Cyanamide.

$$\left.\begin{array}{l}\mathrm{C}^{\mathrm{IV}}\\ \mathrm{C}^{\mathrm{IV}}\\ \mathrm{C}^{\mathrm{IV}}\\ \mathrm{H}^6\end{array}\right\}\mathrm{N}^6$$

Melamine.

$$\left.\begin{array}{l}\mathrm{C}^{\mathrm{IV}}\\ \mathrm{C}^{\mathrm{IV}}\\ \mathrm{CO}''\\ \mathrm{H}^5\end{array}\right\}\mathrm{N}^5$$

Ammeline.

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| | |
|---|---|
| $Cy^3\left\{\begin{matrix}NH^2\\OH\\OH\end{matrix}\right. = (CN)^3\left\{\begin{matrix}NH^2\\OH\\OH\end{matrix}\right.$<br>Ammelid. | $\left.\begin{matrix}(CO'')^2\\C^{IV}\\H^4\end{matrix}\right\}N^4$<br>Ammelid. |
| $Cy^3\left\{\begin{matrix}NH^2\\SH\\SH\end{matrix}\right. = (CN)^3\left\{\begin{matrix}NH^2\\SH\\SH\end{matrix}\right.$<br>Sulphomellonic acid. | $\left.\begin{matrix}(CS'')^2\\C^{IV}\\H^4\end{matrix}\right\}N^4$<br>Sulphomellonic acid. |
| $Cy^3\left\{\begin{matrix}NH^2\\NH^2\\Cl\end{matrix}\right. = (CN)^3\left\{\begin{matrix}NH^2\\NH^2\\Cl\end{matrix}\right.$<br>Chloro-cyanamide. | $\left.\begin{matrix}C''H^3\\C^{IV}H\\C^{IV}Cl\end{matrix}\right\}N^5$<br>Chloro-cyanamide. |
| $\left.\begin{matrix}(Cy^2)^3\\H^3\end{matrix}\right\}N^8 = \left.\begin{matrix}[(CN)^2]^3\\H^3\end{matrix}\right\}N^3$<br>Hydromellon. | $\left.\begin{matrix}(C^{IV})^2H\\(C^{IV})^2H\\(C^{IV})^2H\end{matrix}\right\}N^9$<br>Hydromellon. |
| $\left.\begin{matrix}(Cy^2)^3\\H\\M'^2\end{matrix}\right\}N^3 = \left.\begin{matrix}[(CN)^2]^3\\H\\M'^2\end{matrix}\right\}N^8$<br>Mellonides. | $\left.\begin{matrix}(C^{IV})^2H\\(C^{IV})^2M'\\(C^{IV})^2M'\end{matrix}\right\}N^9$<br>Mellonides. |
| $(Cy^2)^3\left\{\begin{matrix}N'''\\OH\\OH\\OH\end{matrix}\right. = ([CN]^2)^3\left\{\begin{matrix}N'''\\OH\\OH\\OH\end{matrix}\right.$<br>Cyameluric acid. | $\left.\begin{matrix}C^{IV}.CO''.H\\C^{IV}.CO''.H\\C^{IV}.CO''.H\end{matrix}\right\}N^7$*<br>Cyameluric acid. |
| $Cy^3N = (CN)^3N$<br>Tricyanamide (unknown). | $\left.\begin{matrix}C^{IV}\\C^{IV}\\C^{IV}\end{matrix}\right\}N^4$<br>Tricyanamide (unknown). |
| $\left.\begin{matrix}Cy^3\\Cy^3\\Cy^3\end{matrix}\right\}N^3 = \left.\begin{matrix}(CN)^3\\(CN)^3\\(CN)^3\end{matrix}\right\}N^3$<br>Polymer of tricyanamide (unknown). | $\left.\begin{matrix}(C^{IV})^3\\(C^{IV})^3\\(C^{IV})^3\end{matrix}\right\}N^{12}$<br>Polymer of tricyanamide (unknown). |

## CARBONIC AMIDES.

When speaking of lactic and analogous acids, we said that, besides two isomeric monamides, each of these acids should be able to give rise to a diamide, but that, up to the present time, none of these diamides could be prepared. Moreover, we saw that carbonic acid, the first

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* In the first edition the formula ($C^6H^4N^8O^2$) proposed by Gerhardt for cyameluric acid was adopted. But since then Liebig has shown that the true formula of this body is ($C^6H^3N^7O^3$). If Gerhardt's formula were correct, the rational formula of this acid would be—

$$(Cy^2)^3\left\{\begin{matrix}(NH)''\\(NH)''\\(OH)'\\(OH)'\end{matrix}\right. = ([CN]^2)^3\left\{\begin{matrix}(NH)''\\(NH)''\\(OH)'\\(OH)'\end{matrix}\right. \text{ or } \left.\begin{matrix}(CO'')^2.H^4\\C^{IV2}\\C^{IV2}\end{matrix}\right\}N^8$$

term of the series to which lactic acid belongs, differs from its homologues; that it is not biatomic and monobasic like these, but biatomic and bibasic.

Now biatomic and bibasic acids are capable of giving neutral diamides, amic acids, and imides.

We may therefore expect three ammoniacal derivatives of carbonic acid: $\left(\left.\begin{matrix}CO''\\H^2\end{matrix}\right\}O^2\right)$.

1st. Carbamic acid . . . $\left.\begin{matrix}\left[\left.\begin{matrix}CO''\\H\end{matrix}\right\}O\right]'\\H^2\end{matrix}\right\}N$

2nd. Carbimide . . . . $\left.\begin{matrix}CO''\\H\end{matrix}\right\}N$

3rd. Carbo-diamide . . . $\left.\begin{matrix}CO''\\H^2\\H^2\end{matrix}\right\}N^2$

Other derivatives, such as dicarbo-triamide $\left(\left.\begin{matrix}CO''\\CO''\\H^5\end{matrix}\right\}N^3\right)$, etc., belonging to more condensed types, may also be looked for.

Carbamic acid has not as yet been obtained in a free state, but an ammoniacal salt of this acid is formed when carbonic anhydride acts on ammoniacal gas:

$$\underset{\text{Carbonic anhydride.}}{(CO''O)} \quad + \quad \underset{\text{Ammonia.}}{2(NH^3)} \quad = \quad \underset{\text{Carbamate of ammonium.}}{\left(\left.\begin{matrix}\left[\left.\begin{matrix}CO''\\NH^4\end{matrix}\right\}O\right]\\H\\H\end{matrix}\right\}N\right)}$$

Bodies are also known which only differ from carbonic acid by the substitution of a radicle of alcohol or phenol for an atom of hydrogen. Such is phenyl-carbamic or anthranilic acid $\left(\left.\begin{matrix}\left[\left.\begin{matrix}CO''\\H\end{matrix}\right\}O\right]\\C^6H^5\\H\end{matrix}\right\}N\right)$, which is obtained by the action of potash on indigo.

Carbonic imide $\left(\left.\begin{matrix}CO''\\H\end{matrix}\right\}N\right)$ is probably identical with cyanic acid.

Carbo-diamide $\left(\left.\begin{matrix}CO''\\H^4\end{matrix}\right\}N^2\right)$ also exists; it is known as urea. Its four atoms of hydrogen may be replaced by radicles of acids or of alcohols, in which case compound ureas are produced.

Lastly, there is the dicarbo-triamide $\left(\left.\begin{matrix}(CO'')^2\\H^5\end{matrix}\right\}N^3\right)$, known as *biuret*, which is formed when urea is submitted to a temperature of 170° for some time.

Of all the carbonic amides, the only ones possessing much interest are carbo-diamide and its derivatives, that is to say the ureas, comprising under this general title both simple urea and the compound ureas.

## UREAS.

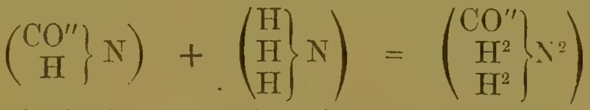
### SIMPLE UREA.

Urea exists ready formed in urine, from which it may be extracted by the following process:

The urine is evaporated to about the sixth part of its volume, then nitric acid, free from nitrous products, is added to the syrupy liquid. A sparingly soluble compound of nitric acid and urea (nitrate of urea) is formed, and precipitated along with some colouring matters. This precipitate after being collected on a filter, is dissolved in boiling water, powdered animal black being added, and the hot liquid is filtered. Perfectly white nitrate of urea is deposited on cooling. In order to extract the urea from this salt, it is dissolved in boiling water, and barytic carbonate is added to the solution, which is filtered in order to separate any excess of the carbonate, and then crystallized; the barytic nitrate first crystallizes and then the urea. To remove the last traces of the former from the urea, it is crystallized from alcohol, which does not dissolve the barytic salt.

Urea may also be obtained synthetically, and by several different processes.

*First Process.*—Cyanic acid is combined with ammonia, or what comes to the same thing, solutions of ammonic sulphate and potassic cyanate are mixed; urea is then produced by double decomposition:

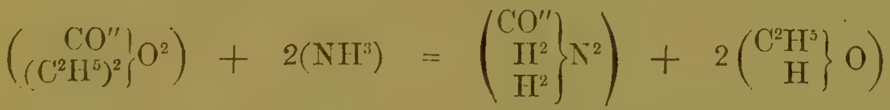


$$\left(\left.\begin{matrix}CO''\\H\end{matrix}\right\}N\right) + \left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right) = \left(\left.\begin{matrix}CO''\\H^2\\H^2\end{matrix}\right\}N^2\right)$$

Cyanic acid. Ammonia. Urea.

It is very easy to understand this method of preparation, if it be remembered that cyanic acid is a carbonic imide. It has been seen, moreover, that the imides are derived from diamides (*see* Amides) by the elimination of ammonia, and that, on the other hand, the diamides may be prepared by fixing ammonia on the imides.

*Second Process.*—Ammonia is made to act on the carbonate of ethyl:

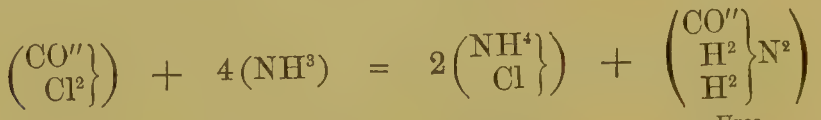


$$\left(\left.\begin{matrix}CO''\\(C^2H^5)^2\end{matrix}\right\}O^2\right) + 2(NH^3) = \left(\left.\begin{matrix}CO''\\H^2\\H^2\end{matrix}\right\}N^2\right) + 2\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)$$

Carbonate of ethyl. Ammonia. Urea. Alcohol.

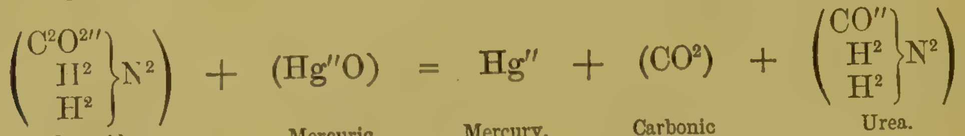
These two bodies should be heated for some time in a hermetically-sealed tube.

*Third Process.*—Urea is also produced in the reaction of ammoniacal gas on the chloride of carbonyl; chloride of ammonium is formed at the same time. These two bodies are separated by means of absolute alcohol, which dissolves only the urea:



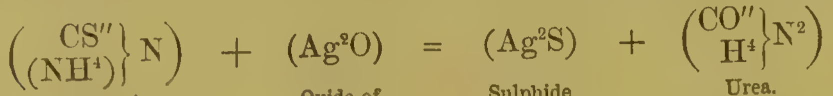
$$\underset{\substack{\text{Chloride of}\\\text{carbonyl.}}}{\left(\left.\begin{matrix}CO''\\Cl^2\end{matrix}\right\}\right)} + \underset{\text{Ammonia.}}{4(NH^3)} = \underset{\substack{\text{Chloride of}\\\text{ammonium.}}}{2\left(\left.\begin{matrix}NH^4\\Cl\end{matrix}\right\}\right)} + \underset{\text{Urea.}}{\left(\left.\begin{matrix}CO''\\H^2\\H^2\end{matrix}\right\}N^2\right)}$$

*Fourth Process.*—Dr. Williamson has obtained urea by heating oxamide with mercuric oxide over a spirit lamp until the mass assumes a greyish appearance, dissolving in boiling water, filtering and crystallizing:



$$\underset{\text{Oxamide.}}{\left(\left.\begin{matrix}C^2O^{2''}\\H^2\\H^2\end{matrix}\right\}N^2\right)} + \underset{\substack{\text{Mercuric}\\\text{oxide.}}}{(Hg''O)} = \underset{\text{Mercury.}}{Hg''} + \underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{(CO^2)} + \underset{\text{Urea.}}{\left(\left.\begin{matrix}CO''\\H^2\\H^2\end{matrix}\right\}N^2\right)}$$

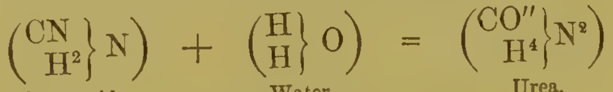
*Fifth Process.*—Urea appears to be produced when a solution of sulphocyanate of ammonium is heated with oxide of silver:



$$\underset{\substack{\text{Ammonic}\\\text{sulphocyanate.}}}{\left(\left.\begin{matrix}CS''\\(NH^4)\end{matrix}\right\}N\right)} + \underset{\substack{\text{Oxide of}\\\text{silver.}}}{(Ag^2O)} = \underset{\substack{\text{Sulphide}\\\text{of silver.}}}{(Ag^2S)} + \underset{\text{Urea.}}{\left(\left.\begin{matrix}CO''\\H^4\end{matrix}\right\}N^2\right)}$$

This reaction yields very little product, because as the urea is formed it is destroyed by the simultaneous action of water and heat.

*Sixth Process.*—Nitrate of urea, and consequently urea, is formed when nitric acid is added to an ethereal solution of cyanamide:



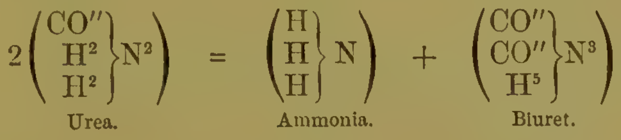
$$\underset{\text{Cyanamide.}}{\left(\left.\begin{matrix}CN\\H^2\end{matrix}\right\}N\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Urea.}}{\left(\left.\begin{matrix}CO''\\H^4\end{matrix}\right\}N^2\right)}$$

Lastly, urea is produced in a number of reactions: by the action of the alkalies on creatine, of nitric acid on allantoin, of oxidizing agents on uric acid, of hydrosulphuric acid on the ammoniacal fulminate of copper, etc.

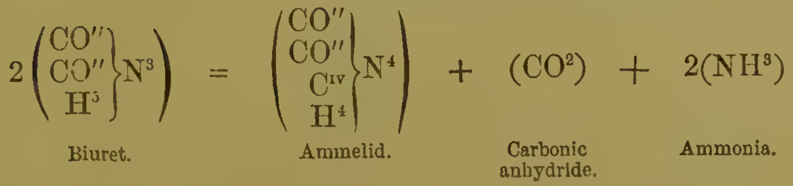
Properties.—1st. Urea crystallizes in prisms with a square base; it is soluble in water and alcohol, and very sparingly so in ether.

2nd. When brought into contact with certain salts containing water of crystallization, it separates this water, and the solid mass becomes pasty. This action is the more singular as urea has no affinity for moisture.

3rd. Under the influence of heat, urea first melts, then disengages ammonia, and leaves a residue of biuret; if greater heat be applied, this latter in its turn loses carbonic anhydride and ammonia, and is transformed into ammelid:

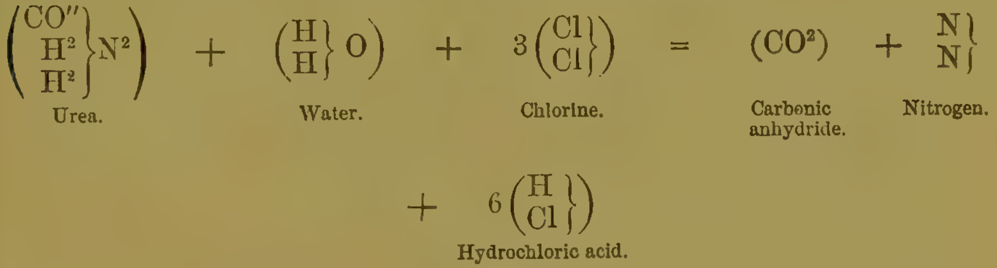


$$2\underset{\text{Urea.}}{\left(\left.\begin{matrix}\mathrm{CO''}\\ \mathrm{H^2}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{N^2}\right)} = \underset{\text{Ammonia.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{N}\right)} + \underset{\text{Biuret.}}{\left(\left.\begin{matrix}\mathrm{CO''}\\ \mathrm{CO''}\\ \mathrm{H^5}\end{matrix}\right\}\mathrm{N^3}\right)}$$

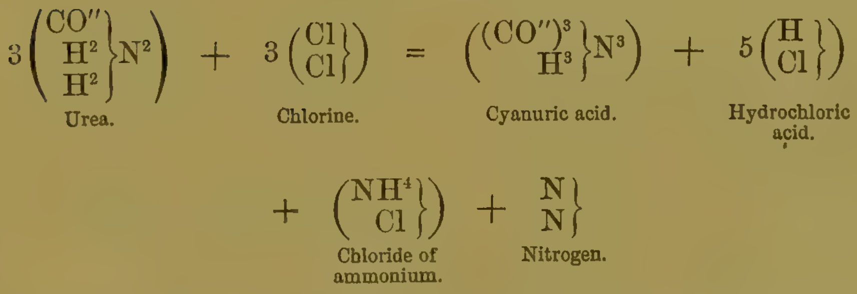


$$2\underset{\text{Biuret.}}{\left(\left.\begin{matrix}\mathrm{CO''}\\ \mathrm{CO''}\\ \mathrm{H^5}\end{matrix}\right\}\mathrm{N^3}\right)} = \underset{\text{Ammelid.}}{\left(\left.\begin{matrix}\mathrm{CO''}\\ \mathrm{CO''}\\ \mathrm{C^{IV}}\\ \mathrm{H^4}\end{matrix}\right\}\mathrm{N^4}\right)} + \underset{\text{Carbonic anhydride.}}{(\mathrm{CO^2})} + \underset{\text{Ammonia.}}{2(\mathrm{NH^3})}$$

4th. Chlorine decomposes an aqueous solution of urea into carbonic anhydride, nitrogen, and hydrochloric acid; but if dry chlorine be transmitted through melted urea, hydrochloric and cyanuric acids, hydrochlorate of ammonia and nitrogen are produced:

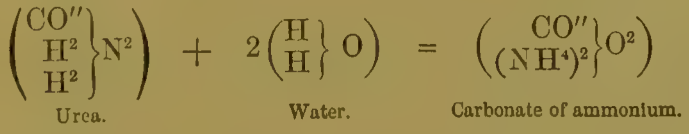


$$\underset{\text{Urea.}}{\left(\left.\begin{matrix}\mathrm{CO''}\\ \mathrm{H^2}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{N^2}\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} + 3\underset{\text{Chlorine.}}{\left(\left.\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right\}\right)} = \underset{\text{Carbonic anhydride.}}{(\mathrm{CO^2})} + \underset{\text{Nitrogen.}}{\left.\begin{matrix}\mathrm{N}\\ \mathrm{N}\end{matrix}\right\}} + 6\underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{Cl}\end{matrix}\right\}\right)}$$



$$3\underset{\text{Urea.}}{\left(\left.\begin{matrix}\mathrm{CO''}\\ \mathrm{H^2}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{N^2}\right)} + 3\underset{\text{Chlorine.}}{\left(\left.\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right\}\right)} = \underset{\text{Cyanuric acid.}}{\left(\left.\begin{matrix}\mathrm{(CO'')^3}\\ \mathrm{H^3}\end{matrix}\right\}\mathrm{N^3}\right)} + 5\underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\text{Chloride of ammonium.}}{\left(\left.\begin{matrix}\mathrm{NH^4}\\ \mathrm{Cl}\end{matrix}\right\}\right)} + \underset{\text{Nitrogen.}}{\left.\begin{matrix}\mathrm{N}\\ \mathrm{N}\end{matrix}\right\}}$$

5th. Urea, when heated with water to a temperature of 140° in a hermetically-sealed tube, absorbs two molecules of this liquid, and is transformed into carbonate of ammonium:



$$\underset{\text{Urea.}}{\left(\left.\begin{matrix}\mathrm{CO''}\\ \mathrm{H^2}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{N^2}\right)} + 2\underset{\text{Water.}}{\left(\left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\text{Carbonate of ammonium.}}{\left(\left.\begin{matrix}\mathrm{CO''}\\ \mathrm{(NH^4)^2}\end{matrix}\right\}\mathrm{O^2}\right)}$$

An analogous reaction takes place when urea is left with the organic ferments produced in urine, or when urea is acted upon by boiling alkalies or acids. In this case, instead of the ammonic carbonate, products of its decomposition by the alkalies or acids are obtained.

6th. Nitrous acid transforms urea into carbonic anhydride, water, and nitrogen :

$$\underset{\text{Urea.}}{\left(\left.\begin{matrix}\mathrm{CO''}\\\mathrm{H^2}\\\mathrm{H^2}\end{matrix}\right\}\mathrm{N^2}\right)} + \underset{\text{Nitrous acid.}}{2\left(\left.\begin{matrix}\mathrm{NO}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\text{Nitrogen.}}{2\left(\left.\begin{matrix}\mathrm{N}\\\mathrm{N}\end{matrix}\right\}\right)} + \underset{\text{Carbonic anhydride.}}{(\mathrm{CO''},\mathrm{O})}$$

$$+ \underset{\text{Water.}}{3\left(\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\right)}$$

These two latter reactions of urea might be foreseen; they are identical with those produced with all the amides.

7th. A mixture of solutions of urea and of nitrate of silver is converted by evaporation into nitrate of ammonium and cyanate of silver. This fact is not surprising, as though urea does not possess the properties either of the cyanates or of the ammoniacal salts, it has the composition of cyanate of ammonium :

$$\underset{\text{Urea.}}{\left(\left.\begin{matrix}\mathrm{CO''}\\\mathrm{H^2}\\\mathrm{H^2}\end{matrix}\right\}\mathrm{N^2}\right)} + \underset{\text{Nitrate of silver.}}{\left(\left.\begin{matrix}\mathrm{NO^{2\prime}}\\\mathrm{Ag}\end{matrix}\right\}\mathrm{O}\right)} = \underset{\text{Cyanate of silver.}}{\left(\left.\begin{matrix}\mathrm{CO''}\\\mathrm{Ag}\end{matrix}\right\}\mathrm{N}\right)} + \underset{\text{Ammonic nitrate.}}{\left(\left.\begin{matrix}\mathrm{NO^{2\prime}}\\\mathrm{NH^4}\end{matrix}\right\}\mathrm{O}\right)}$$

8th. Urea unites directly with acids in the same way as the alkaloids; it does not, however, combine either with lactic, uric, or hippuric acid.

Though derived from two molecules of ammonia, urea manifests mon-acid properties. A single molecule of nitric or hydrochloric acid is sufficient to saturate it.

Urea may also unite with salts, properly so called, instead of with acids ; thus, besides the nitrate of urea ($CH^4N^2O,NHO^3$), there exists a combination of urea and sodic nitrate ($CH^4N^2O,NNaO^3$) ; besides the hydrochlorate of urea ($CH^4N^2O,HCl$), there is the chloride of sodium and urea ($CH^4N^2O,NaCl$), etc.

9th. Urea also combines with certain metallic oxides, such as mercuric oxide or oxide of silver ; for instance, the compounds ($CH^4N^2O,Hg''O$) ; [$(CH^4N^2O)^2(Hg''O)^2$] ; ($CH^4N^2O(Hg''O)^3$) ; [$(CH^4N^2O)^2(Ag^2O)^3$] are known.

Determination of the Proportion of Urea contained in Urine.—Several methods have been proposed for this object. The following are the principal :

1st. M. Heintz weighs a quantity of fresh, cold urine contained in a glass having a capacity of 25 cubic centimetres. He divides this urine into two parts, to the first of which, weighing from 6 to 8 grammes, he adds a few drops of hydrochloric acid, and sets it aside for twenty-four hours in a cool place. Uric acid is deposited, and is separated by filtration. Six grammes of sulphuric acid are added to the filtered liquid, which is put into a platinum crucible and gently evaporated until gas begins to be disengaged. The crucible is then covered with a watch-glass and heated until the acid vapours completely fill it. The temperature may be carried as high as 180°.

When the reaction is completed, the liquid is filtered into a porcelain capsule, and evaporated almost to dryness, and hydrochloric acid and platinic chloride are added to the residue. The precipitate is collected on a filter, and, when well washed, is dried and weighed. This gives the weight of the double chloride of ammonium and platinum, arising from the sulphate of ammonium formed by the decomposition of the urea and the ammoniacal salts existing in the urine, combined with the weight of the double chloride of platinum and potassium arising from the potassic salts contained in the urine.

The second portion of the urine is precipitated by platinic chloride. The precipitate is collected and washed with the usual precautions; it contains double chlorides formed at the expense of the potassic and ammoniacal salts of the urine. It is evident that if we deduct its weight (of course reduced by calculation to the same quantity of urine) from that of the first precipitate, the difference will give the quantity of the platino-ammoniacal chloride which accrues from the urea. Then the weight of this urea decomposed may be easily calculated; we have only to remember that two molecules of the double chloride correspond to one molecule of urea.

2nd. M. Bunsen recommends a known weight of urine to be saturated with a great excess of chloride of barium, the precipitate due to the salts contained in the urine to be removed by filtration, and the liquid to be heated to between 220° and 240° in a hermetically-sealed tube. The carbonate of ammonium which is formed gives, in presence of the chloride of barium, a precipitate of barytic carbonate, from the weight of which that of the urea may be deduced; in fact, each molecule of this salt represents a molecule of urea.

3rd. M. Millon determines the proportion of urea by means of its decomposition by nitrous acid. He treats 15 or 20 grammes of urine by an acid solution of mercuric nitrate containing nitrous fumes. He transmits the gases which disengage, first over pumice-stone moistened with sulphuric acid to absorb the nitrous vapours, then into a tube with Liebig's bulbs containing a solution of potash to retain the carbonic anhydride. The weight of the urea is ascertained by multiplying that of the carbonic anhydride obtained by 1·3636.

4th. M. Lecomte has recourse to the action exercised by chlorine on an aqueous solution of urea. He places the urine in a small globe from which the air is displaced by means of a current of carbonic acid gas, then he transmits a current of chlorine into the globe, which is gently heated. The gases which disengage are received into a bell-glass containing a solution of potash, over mercury, to absorb the hydrochloric acid, carbonic anhydride, and excess of chlorine. At the close of the operation all the nitrogen contained in the apparatus is displaced by again transmitting carbonic acid gas into it, and the nitrogen contained in the small bell-glass is measured. Knowing the density of the nitrogen, its weight is deduced from its volume, and by means of this weight that of the urea is calculated. We know that $N^2$ correspond to a molecule of this body, that is to say, that 28 parts by weight of nitrogen represent 60 parts of urea.

5th. M. Liebig prepares a normal volumetric solution of mercuric nitrate without excess of acid, and adds this to the urine until precipitation ceases. From the quantity of the solution employed he deduces the quantity of the urea, having first ascertained the quantity required to precipitate a known weight of pure urea from its solution in water.

In this process, however, the precipitation is not complete, because the acid which is liberated at the same time retains a portion of the urea in solution. In order to obviate this, when precipitation ceases the liquid must be exactly saturated with baryta water, more of the mercuric nitrate added, and so on till it finally ceases to produce any precipitation.

M. Liebig's process may be used to extract urea from the blood. After separating the clot which forms spontaneously, and coagulating the albumen by heat, the liquid is filtered and the urea precipitated from it by means of the mercuric nitrate. The precipitate is collected on a filter and washed, and then suspended in water and decomposed by a current of sulphuretted hydrogen. Sulphide of mercury is thrown down, and the urea remains in solution: after filtering, the proportion of the urea is ascertained by one of the above-mentioned processes. It could not be at once determined in the serum, as this contains too small a quantity, and therefore must first be concentrated.

## COMPOUND UREAS.

Compound ureas are those bodies which represent urea the hydrogen of which is wholly or partly replaced by radicles of alcohols or of acids.

The compound ureas having alcohol radicles may contain radicles of monatomic alcohols, in which case they belong to the same type as urea; or they may contain radicles of polyatomic alcohols, when they belong to a more condensed type.

We must therefore consider: 1st, those which, like simple urea, belong to the type $N^2H^6$; and secondly, those belonging to a more condensed type.

### Ureas belonging to the Type $N^2H^6$.

Among these, there are some which contain the radicles of alcohols, and some are known containing sulphur and phosphorus among their elements.

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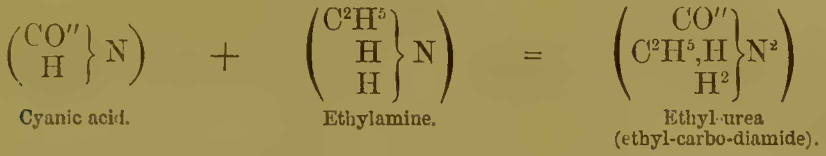
### *Ureas which contain Radicles of Alcohols.*

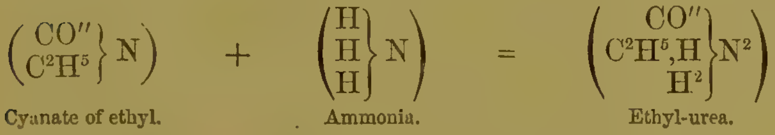
One, two, three, or four atoms of the hydrogen of ordinary urea may be replaced by radicles of monatomic alcohols; thence ureas of the first, second, third, or fourth degree.

In order to denominate the compound ureas, the word urea is preceded by the name of the radicle or radicles which enter into their composition, and these radicles are themselves preceded by the syllables *di*, *tri*, *tetra*, to indicate the number of molecules of each of them. Thus we say ethyl-urea, diethyl-urea, ethyl-amyl-urea, tetrethyl-urea, etc.

**Mon-alcoholic Ureas.**—PREPARATION.—These ureas are prepared either by causing cyanic acid to act on primary monamines, or by causing ammonia to act on the cyanic ethers:

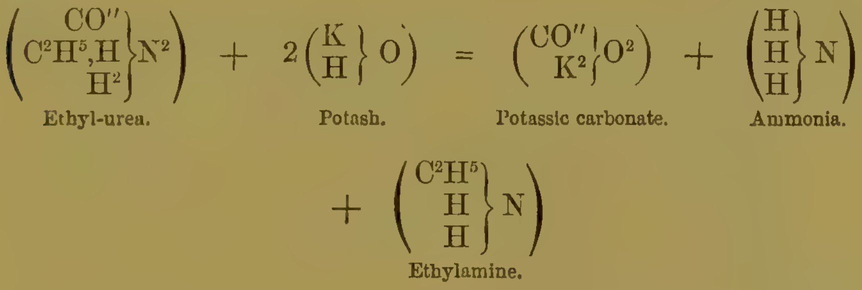


$$\underset{\text{Cyanic acid.}}{\left(\left.\begin{matrix}CO''\\ H\end{matrix}\right\}N\right)} + \underset{\text{Ethylamine.}}{\left(\left.\begin{matrix}C^2H^5\\ H\\ H\end{matrix}\right\}N\right)} = \underset{\substack{\text{Ethyl-urea}\\ \text{(ethyl-carbo-diamide).}}}{\left(\left.\begin{matrix}CO''\\ C^2H^5,H\\ H^2\end{matrix}\right\}N^2\right)}$$



$$\underset{\text{Cyanate of ethyl.}}{\left(\left.\begin{matrix}CO''\\ C^2H^5\end{matrix}\right\}N\right)} + \underset{\text{Ammonia.}}{\left(\left.\begin{matrix}H\\ H\\ H\end{matrix}\right\}N\right)} = \underset{\text{Ethyl-urea.}}{\left(\left.\begin{matrix}CO''\\ C^2H^5,H\\ H^2\end{matrix}\right\}N^2\right)}$$

PROPERTIES.—When treated with alkalies, these ureas give an alkaline carbonate and disengage a mixture of ammonia and a primary monamine:

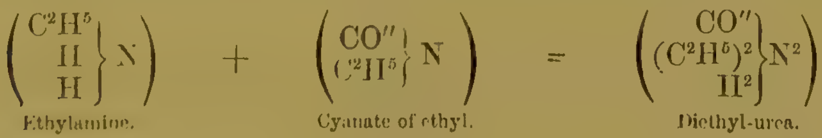


$$\underset{\text{Ethyl-urea.}}{\left(\left.\begin{matrix}CO''\\ C^2H^5,H\\ H^2\end{matrix}\right\}N^2\right)} + 2\underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\ H\end{matrix}\right\}O\right)} = \underset{\text{Potassic carbonate.}}{\left(\left.\begin{matrix}CO''\\ K^2\end{matrix}\right\}O^2\right)} + \underset{\text{Ammonia.}}{\left(\left.\begin{matrix}H\\ H\\ H\end{matrix}\right\}N\right)}$$

$$+ \underset{\text{Ethylamine.}}{\left(\left.\begin{matrix}C^2H^5\\ H\\ H\end{matrix}\right\}N\right)}$$

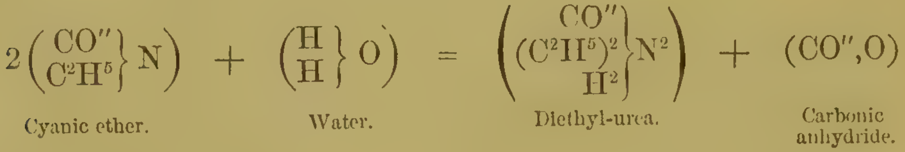
According to M. Volhard, the ureas obtained by the action of cyanic acid on primary monamines, and those obtained by treating the cyanic ethers by ammonia, are not identical though they are resolved into the same products under the influence of potash; there will be found certain physical differences between them.

**Di-alcoholic Ureas.**—PREPARATION.—*First Process.*—These ureas may be obtained by causing a primary monamine to act on a cyanic ether:



$$\underset{\text{Ethylamine.}}{\left(\left.\begin{matrix}C^2H^5\\ H\\ H\end{matrix}\right\}N\right)} + \underset{\text{Cyanate of ethyl.}}{\left(\left.\begin{matrix}CO''\\ C^2H^5\end{matrix}\right\}N\right)} = \underset{\text{Diethyl-urea.}}{\left(\left.\begin{matrix}CO''\\ (C^2H^5)^2\\ H^2\end{matrix}\right\}N^2\right)}$$

*Second Process.*—They may also be obtained by treating the cyanic ethers with water:

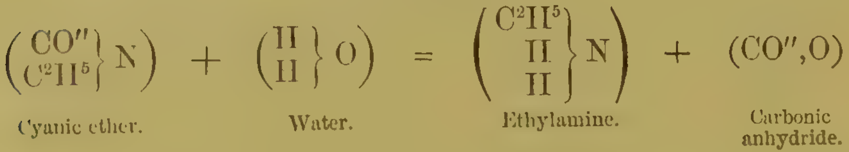


$$2\underset{\text{Cyanic ether.}}{\left(\left.\begin{matrix}CO''\\C^2H^5\end{matrix}\right\}N\right)}+\underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}=\underset{\text{Diethyl-urea.}}{\left(\left.\begin{matrix}CO''\\(C^2H^5)^2\\H^2\end{matrix}\right\}N^2\right)}+\underset{\text{Carbonic anhydride.}}{(CO'',O)}$$

It is probable that this reaction is accomplished in two stages; first a molecule of cyanic ether is transformed, under the influence of water, into primary monamine and carbonic anhydride, and then the primary monamine unites with a second molecule of cyanic ether to form a dialcoholic urea:

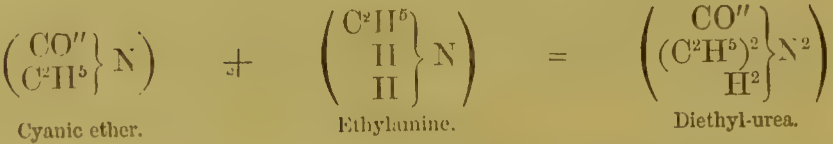
### FIRST STAGE.

LEEDS



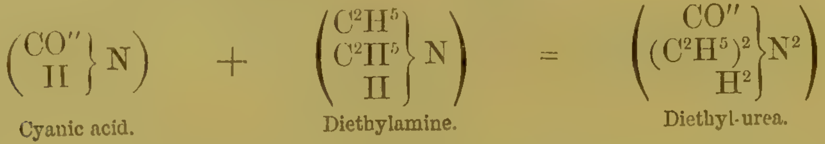
$$\underset{\text{Cyanic ether.}}{\left(\left.\begin{matrix}CO''\\C^2H^5\end{matrix}\right\}N\right)}+\underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}=\underset{\text{Ethylamine.}}{\left(\left.\begin{matrix}C^2H^5\\H\\H\end{matrix}\right\}N\right)}+\underset{\text{Carbonic anhydride.}}{(CO'',O)}$$

### SECOND STAGE.



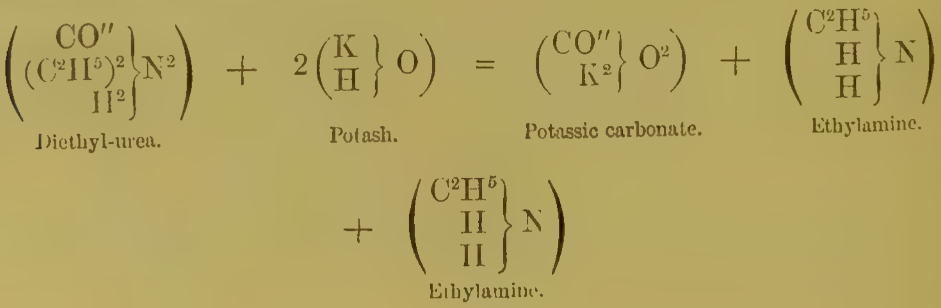
$$\underset{\text{Cyanic ether.}}{\left(\left.\begin{matrix}CO''\\C^2H^5\end{matrix}\right\}N\right)}+\underset{\text{Ethylamine.}}{\left(\left.\begin{matrix}C^2H^5\\H\\H\end{matrix}\right\}N\right)}=\underset{\text{Diethyl-urea.}}{\left(\left.\begin{matrix}CO''\\(C^2H^5)^2\\H^2\end{matrix}\right\}N^2\right)}$$

*Third Process.*—These compounds may also be prepared by the action of a secondary monamine on cyanic acid:



$$\underset{\text{Cyanic acid.}}{\left(\left.\begin{matrix}CO''\\H\end{matrix}\right\}N\right)}+\underset{\text{Diethylamine.}}{\left(\left.\begin{matrix}C^2H^5\\C^2H^5\\H\end{matrix}\right\}N\right)}=\underset{\text{Diethyl-urea.}}{\left(\left.\begin{matrix}CO''\\(C^2H^5)^2\\H^2\end{matrix}\right\}N^2\right)}$$

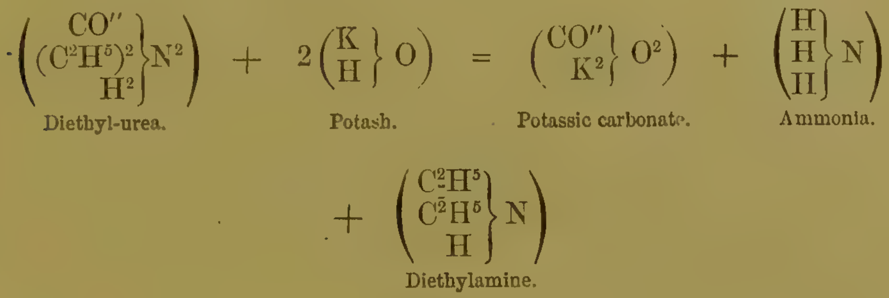
PROPERTIES.—1st. Under the influence of alkalies, the ureas obtained by the action of cyanic ethers on primary monamines are resolved into an alkaline carbonate and two molecules of primary monamines:



$$\underset{\text{Diethyl-urea.}}{\left(\left.\begin{matrix}CO''\\(C^2H^5)^2\\H^2\end{matrix}\right\}N^2\right)}+2\underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)}=\underset{\text{Potassic carbonate.}}{\left(\left.\begin{matrix}CO''\\K^2\end{matrix}\right\}O^2\right)}+\underset{\text{Ethylamine.}}{\left(\left.\begin{matrix}C^2H^5\\H\\H\end{matrix}\right\}N\right)}$$
$$+\underset{\text{Ethylamine.}}{\left(\left.\begin{matrix}C^2H^5\\H\\H\end{matrix}\right\}N\right)}$$

2nd. The ureas obtained by the action of water on cyanic ethers act in the same manner under the influence of the alkalies, which fact supports our view of their mode of formation.

3rd. The ureas obtained by means of secondary monamines and cyanic acid are decomposed by alkalies into alkaline carbonate, ammonia and secondary monamines:



$$\underset{\text{Diethyl-urea.}}{\left(\left.\begin{array}{c}CO''\\(C^2H^5)^2\\H^2\end{array}\right\}N^2\right)} + \underset{\text{Potash.}}{2\left(\left.\begin{array}{c}K\\H\end{array}\right\}O\right)} = \underset{\text{Potassic carbonate.}}{\left(\left.\begin{array}{c}CO''\\K^2\end{array}\right\}O^2\right)} + \underset{\text{Ammonia.}}{\left(\left.\begin{array}{c}H\\H\\H\end{array}\right\}N\right)} + \underset{\text{Diethylamine.}}{\left(\left.\begin{array}{c}C^2H^5\\C^2H^5\\H\end{array}\right\}N\right)}$$

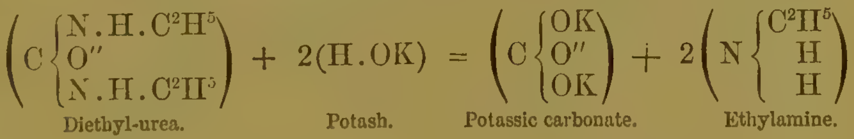
The differences observed between ureas belonging to the same degree of substitution, according to the manner in which they have been prepared, tend to prove that in these bodies the cyanic group and the ammoniacal group remain more or less distinct. Under the influence of alkalies, the ammoniacal group becomes free, and the cyanic group is decomposed as if it were alone.

When the urea contains cyanate of ethyl as the cyanic group, and ethylamine as the ammoniacal compound, the potash first splits it up into ethylamine and cyanate of ethyl. The latter is then decomposed, producing alkaline carbonate and liberating a second molecule of ethylamine.

If, on the contrary, the urea contain cyanic acid and diethylamine, this secondary monamine is first separated from the cyanic acid and then the potash decomposes this latter body, giving rise to potassic carbonate and ammonia. Instead of two molecules of ethylamine being formed as in the preceding case, one molecule of diethylamine and one of ammonia are obtained.

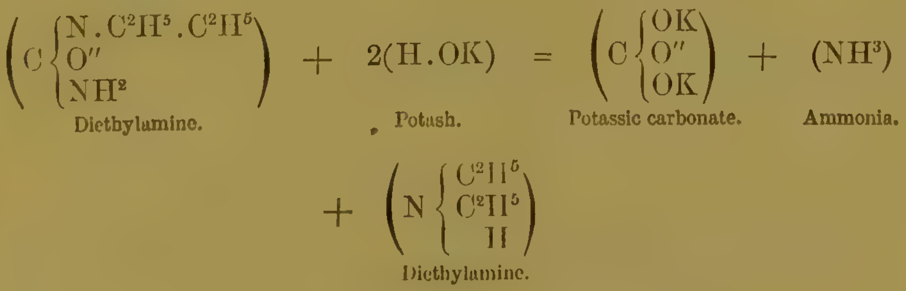
This isomerism may be expressed by the following formulæ:

1st.



$$\underset{\text{Diethyl-urea.}}{\left(C\left\{\begin{array}{l}N.H.C^2H^5\\O''\\N.H.C^2H^5\end{array}\right.\right)} + \underset{\text{Potash.}}{2(H.OK)} = \underset{\text{Potassic carbonate.}}{\left(C\left\{\begin{array}{l}OK\\O''\\OK\end{array}\right.\right)} + \underset{\text{Ethylamine.}}{2\left(N\left\{\begin{array}{c}C^2H^5\\H\\H\end{array}\right.\right)}$$

2nd.



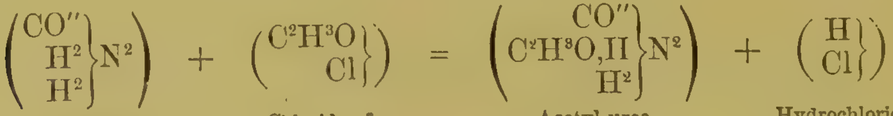
$$\underset{\text{Diethylamine.}}{\left(C\left\{\begin{array}{l}N.C^2H^5.C^2H^5\\O''\\NH^2\end{array}\right.\right)} + \underset{\text{Potash.}}{2(H.OK)} = \underset{\text{Potassic carbonate.}}{\left(C\left\{\begin{array}{l}OK\\O''\\OK\end{array}\right.\right)} + \underset{\text{Ammonia.}}{(NH^3)} + \underset{\text{Diethylamine.}}{\left(N\left\{\begin{array}{c}C^2H^5\\C^2H^5\\H\end{array}\right.\right)}$$

**Tri-alcoholic Ureas.**—No urea of this order is known as yet. M. Wurtz believed he had obtained one by causing diethylamine to act on cyanic ether, but afterwards he perceived that the product obtained was diethyl-urea, formed by the reaction of cyanate of ethyl on the water contained in the diethylamine. Perhaps trialcoholic ureas might be obtained by heating dialcoholic ureas with a hydriodic ether.

**Tetr-alcoholic Ureas.**—M. Hofmann appears to have obtained the tetrethyl-urea by treating cyanic acid with the hydrate of tetrethyl-ammonium. The properties of this body are unknown.

### *Ureas having Acid Radicles.*

Preparation.—M. Zinin has succeeded in substituting acid radicles for an atom of hydrogen in urea, by heating this body with an acid chloride:



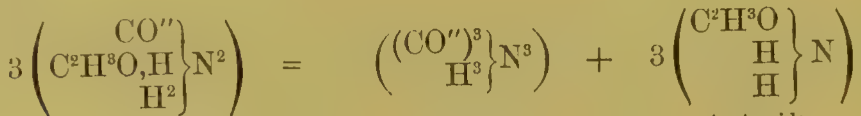
$$\left(\left.\begin{matrix}CO''\\H^2\\H^2\end{matrix}\right\}N^2\right) + \left(\left.\begin{matrix}C^2H^3O\\Cl\end{matrix}\right\}\right) = \left(\left.\begin{matrix}CO''\\C^2H^3O,H\\H^2\end{matrix}\right\}N^2\right) + \left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)$$

Urea. Chloride of acetyl. Acetyl-urea. Hydrochloric acid.

We have already seen that M. Poensgen has obtained cyanurea by a similar process, viz., by heating urea with iodide of cyanogen.

Up to the present time no ureas have been obtained in which more than one atom of hydrogen is replaced by acid radicles.

Properties.—When an urea having an acid radicle is heated, it splits up into cyanuric acid and an amide of the acid which the urea contained:

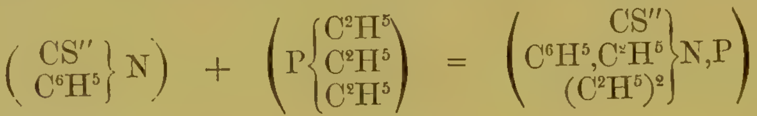


$$3\left(\left.\begin{matrix}CO''\\C^2H^3O,H\\H^2\end{matrix}\right\}N^2\right) = \left(\left.\begin{matrix}(CO'')^3\\H^3\end{matrix}\right\}N^3\right) + 3\left(\left.\begin{matrix}C^2H^3O\\H\\H\end{matrix}\right\}N\right)$$

Acetyl-urea. Cyanuric acid. Acetamide.

### *Sulphuretted and Phosphuretted Ureas.*

By substituting, in the preparation of compound ureas, a sulphocyanic ether for the cyanic ethers and a phosphine for the amines, M. Hofmann has obtained an urea having four alcohol radicles, the oxygen of which is replaced by sulphur and half the nitrogen by phosphorus:

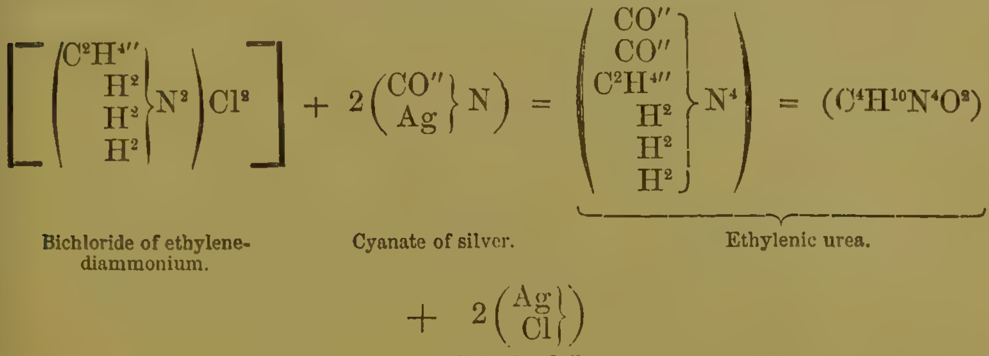


$$\left(\left.\begin{matrix}CS''\\C^6H^5\end{matrix}\right\}N\right) + \left(P\left\{\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right.\right) = \left(\left.\begin{matrix}CS''\\C^6H^5,C^2H^5\\(C^2H^5)^2\end{matrix}\right\}N,P\right)$$

Sulphocyanate of phenyl. Triethyl-phosphine.

### Ureas belonging to a more Condensed Type.

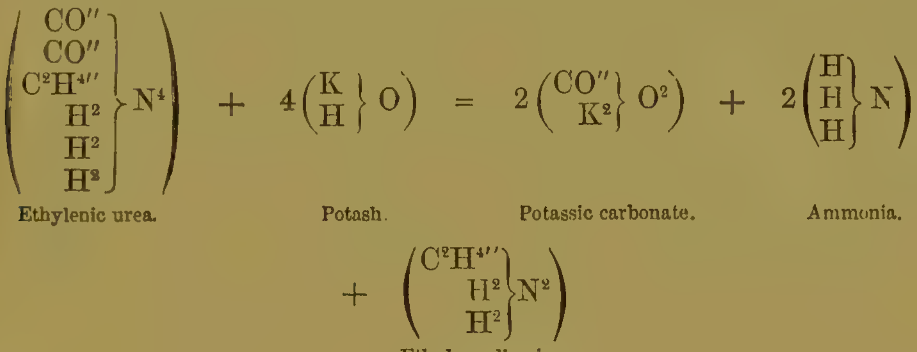
On treating bichloride of ethylene diammonium with cyanate of silver, and separating the product from the insoluble chloride of silver by means of water and alcohol, M. Volhard has obtained ethylenic urea, which is formed by the union of two molecules of cyanic acid with one molecule of ethylene diamine:



$$\left[\left(\left.\begin{matrix}C^2H^{4''}\\H^2\\H^2\\H^2\end{matrix}\right\}N^2\right)Cl^2\right] + 2\left(\left.\begin{matrix}CO''\\Ag\end{matrix}\right\}N\right) = \underbrace{\left(\left.\begin{matrix}CO''\\CO''\\C^2H^{4''}\\H^2\\H^2\\H^2\end{matrix}\right\}N^4\right) = (C^4H^{10}N^4O^2)}_{\text{Ethylenic urea.}} + 2\left(\left.\begin{matrix}Ag\\Cl\end{matrix}\right\}\right)$$

Bichloride of ethylene-diammonium. Cyanate of silver. Ethylenic urea. Chloride of silver.

Under the influence of potash, this urea is transformed into potassic carbonate, ammonia and ethylene-diamine:

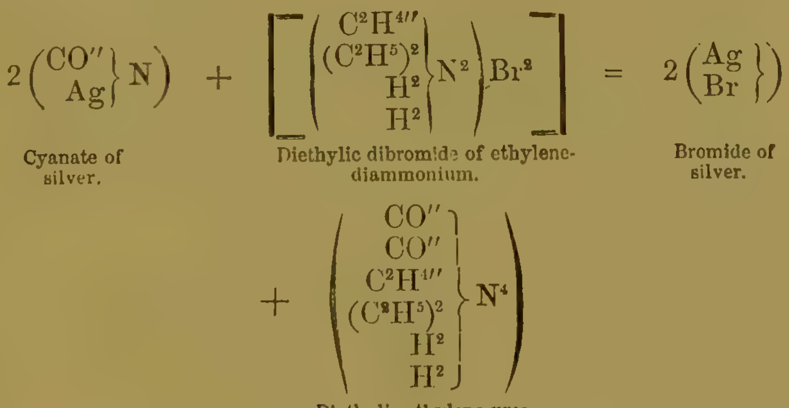


$$\left(\left.\begin{matrix}CO''\\CO''\\C^2H^{4''}\\H^2\\H^2\\H^2\end{matrix}\right\}N^4\right) + 4\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right) = 2\left(\left.\begin{matrix}CO''\\K^2\end{matrix}\right\}O^2\right) + 2\left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right) + \left(\left.\begin{matrix}C^2H^{4''}\\H^2\\H^2\end{matrix}\right\}N^2\right)$$

Ethylenic urea. Potash. Potassic carbonate. Ammonia. Ethylene-diamine.

Ethylenic urea combines with hydrochloric acid in presence of platinic chloride, and gives rise to a double chloride whose formula is $[(C^4H^{10}N^4O^2)^2(HCl)^2,PtCl^4]$. Though derived from four molecules of ammonia, this urea retains the characters of a simple molecule of ammonia; it is a mon-acid tetramine.

On submitting cyanate of silver to the action of diethylic dibromide of ethylene-diammonium, M. Volhard has obtained the diethylic-ethylene urea *a* $(C^8H^{18}N^4O^2)$:



$$2\left(\left.\begin{matrix}CO''\\Ag\end{matrix}\right\}N\right) + \left[\left(\left.\begin{matrix}C^2H^{4''}\\(C^2H^5)^2\\H^2\\H^2\end{matrix}\right\}N^2\right)Br^2\right] = 2\left(\left.\begin{matrix}Ag\\Br\end{matrix}\right\}\right) + \left(\left.\begin{matrix}CO''\\CO''\\C^2H^{4''}\\(C^2H^5)^2\\H^2\\H^2\end{matrix}\right\}N^4\right)$$

Cyanate of silver. Diethylic dibromide of ethylene-diammonium. Bromide of silver. Diethylic ethylene-urea.

This urea is decomposed by potash in the same manner as the preceding one, furnishing, like it, diethylic ethylene-diamine, ammonia, and potassic carbonate.

On adding ethylene-diamine to cyanate of ethyl, M. Volhard has obtained an urea which possesses the same composition as the preceding one, diethylic-ethylene urea $\beta$:

$$\left(\left.\begin{matrix}C^2H^{4''}\\H^2\\H^2\end{matrix}\right\}N^2\right) + 2\left(\left.\begin{matrix}CO''\\C^2H^5\end{matrix}\right\}N\right) = \left(\left.\begin{matrix}CO''\\CO''\\C^2H^{4''}\\(C^2H^5)^2\\H^2\\H^2\end{matrix}\right\}N^4\right)$$

Ethylene-diamine. Cyanate of ethyl. Diethylic ethylene-urea.

However, these two substances are not identical; the diethylic ethylene urea $\beta$, instead of giving diethylic ethylene-diamine and ammonia under the influence of alkalies, gives ethylene-diamine and ethylamine:

$$\left(\left.\begin{matrix}CO''\\CO''\\C^2H^{4''}\\(C^2H^5)^2\\H^2\\H^2\end{matrix}\right\}N^4\right) + 4\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right) = 2\left(\left.\begin{matrix}CO''\\K^2\end{matrix}\right\}O^2\right) + 2\left(\left.\begin{matrix}C^2H^5\\H\\H\end{matrix}\right\}N\right)$$

Diethylic ethylene-urea. Potash. Potassic carbonate. Ethylamine.

$$+ \left(\left.\begin{matrix}C^2H^{4''}\\H^2\\H^2\end{matrix}\right\}N^2\right)$$

Ethylene-diamine.

The isomerism observed between these two diethylic-ethlyene ureas, is of the same kind as that we have described between the diethylurea obtained by ethylamine and cyanic ether, and that obtained from cyanic acid and diethylamine.

## QUINONIC GROUP AND ITS HOMOLOGUES.

There exists in the cinchonas an acid, quinic acid ($C^7H^{12}O^6$), which to a certain extent belongs to the benzoic series. M. Lautemann has shown that, under the influence of hydriodic acid, it is transformed into benzoic acid:

First Part.

$$(C^7H^{12}O^6) + 8\left(\left.\begin{matrix}H\\I\end{matrix}\right\}\right) = 4\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + 4\left(\left.\begin{matrix}I\\I\end{matrix}\right\}\right) + (C^7H^{12}O^2)$$

Quinic acid. Hydriodic acid. Water. Iodine. Unknown body.

### SECOND PART.

$$\underset{\text{Unknown body.}}{(C^7H^{12}O^2)} + \underset{\text{Iodine.}}{3\left(\left.\begin{matrix}I\\I\end{matrix}\right\}\right)} = \underset{\text{Hydriodic acid.}}{6\left(\left.\begin{matrix}H\\I\end{matrix}\right\}\right)} + \underset{\text{Benzoic acid.}}{(C^7H^6O^2)}$$

According to M. Lautemann, the production of the intermediate body $C^7H^{12}O^2$ is probable; but it has not been isolated.

When quinic acid is submitted to the action of oxidizing agents, it is transformed into a substance whose formula is $C^6H^4O^2$, and which has received the name of quinone:

$$\underset{\text{Quinic acid.}}{(C^7H^{12}O^6)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} = \underset{\text{Carbonic anhydride.}}{(CO^2)} + \underset{\text{Water.}}{4\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Quinone.}}{(C^6H^4O^2)}$$

Quinone readily fixes $H^2$ under the influence of reducing agents, and is transformed into hydroquinone $C^6H^6O^2$. Quinone and hydroquinone combine and form a compound called green hydroquinone, the formula of which is $C^6H^4O^2,C^6H^6O^2$, and the colour of which resembles that of the wings of the Spanish fly.

In quinone or hydroquinone four atoms of hydrogen may be replaced either separately or simultaneously, by chlorine.

When perchlorinated quinone is treated by potash, the potassic salt of bichloro-quinonic acid is obtained:

$$\underset{\text{Perchloro-quinone.}}{(C^6Cl^4O^2)} + \underset{\text{Potash.}}{4\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Chloride of potassium.}}{2\left(\left.\begin{matrix}K\\Cl\end{matrix}\right\}\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

$$+ \underset{\text{Potassic bichloro-quinonate.}}{\left(\left.\begin{matrix}C^6Cl^2O^2\\K^2\end{matrix}\right\}O^2\right)}$$

There exist two chloroquinonic amides: chloroquinonamide ($C^6Cl^2H^4O^2N^2$), and bichloroquinonamic acid ($C^6H^3Cl^2NO^3$).

Quinonic acid $C^6H^4O^4$ is not known, but its existence cannot be doubted, as its chlorinated derivatives are known.

What are the rational formulæ proper for all these bodies?

According to my idea, quinone is an aldehyd of the second degree, derived from an unknown glycol $C^6H^8O^2$ by elimination of $H^4$, and hydroquinone is an aldehyd of the first degree, derived from the same glycol by elimination of $H^2$ only. According to this hypothesis, the different bodies of which we have spoken take the following formulæ:

Quinone . . . . . . . . . . . . . . $\left.\begin{matrix}C^6H^2O^{2\prime\prime}\\H^2\end{matrix}\right\}$

| | |
|---|---|
| Bichloroquinone or chloride of quinoyl . . . . . | $\left.\begin{matrix}C^6H^2O^{2\prime}\\Cl^{2\prime}\end{matrix}\right\}$ |
| Perchlorinated quinone or perchlorinated chloride of quinoyl . . . . . . . . . . | $\left.\begin{matrix}C^6Cl^2O^{2\prime\prime}\\Cl^2\end{matrix}\right\}$ |
| Quinonic acid . . . . . . . . . . . . | $\left.\begin{matrix}C^6H^2O^{2\prime\prime}\\H^2\end{matrix}\right\}O^2$ |
| Bichloroquinonic acid . . . . . . . . . . | $\left.\begin{matrix}C^6Cl^2O^{2\prime\prime}\\H^2\end{matrix}\right\}O^2$ |
| Quinonine diamide . . . . . . . . . . | $\left.\begin{matrix}C^6H^2O^{2\prime\prime}\\H^2\\H^2\end{matrix}\right\}N^2$ |
| Bichloroquinonic diamide . . . . . . . . | $\left.\begin{matrix}C^6Cl^2O^{2\prime\prime}\\H^2\\H^2\end{matrix}\right\}N^2$ |
| Quinonamic acid . . . . . . . . | $\left.\begin{matrix}\left[\left.\begin{matrix}C^6H^2O^{2\prime\prime}\\H\end{matrix}\right\}O\right]^{\prime}\\H\\H\end{matrix}\right\}N$ |
| Bichloroquinonamic acid . . . . . . | $\left.\begin{matrix}\left[\left.\begin{matrix}C^6Cl^2O^{2\prime\prime}\\H\end{matrix}\right\}O\right]^{\prime}\\H\\H\end{matrix}\right\}N$ |
| Hydroquinone. . . . . . . . . . | $\left.\begin{matrix}\left(\left.\begin{matrix}C^6H^4O^{\prime\prime}\\H\end{matrix}\right\}O\right)^{\prime}\\H\end{matrix}\right\}$ |

Green hydroquinone should be regarded as a simple combination of quinone and hydroquinone, and this combination is easy to imagine, because neither quinone nor hydroquinone are saturated.

If our view of hydroquinone be correct, if this body is an aldehyd, the existence of an acid may be foreseen which should have for formula $\left(\left.\begin{matrix}C^6H^4O^{\prime\prime}\\H^2\end{matrix}\right\}O^2\right) = C^6H^6O^3$, and which would be biatomic and monobasic.

Gerhardt has admitted the formulæ we have given for quinone and the acids derived from it, but he has not proposed one for hydroquinone.

Hydroquinone is isomeric with pyrocatechol (oxyphenic acid).

Two homologues of quinone are known; these are phlorone $C^8H^8O^2$, obtained by the oxidation of ordinary phenol mixed with cresylic phenol, and thymoyl $C^{12}H^{16}O^2$, obtained by the oxidation of thymilic phenol or thymol $C^{10}H^{14}O$.

Bodies which are homologues of hydroquinone and green hydroquinone correspond to phlorone and thymoyl.

It is difficult to explain how the oxidation of cresylic phenol and thymilic phenol can give rise to compounds which are more carburetted than these phenols themselves.

## COMPOUNDS NOT CLASSED IN ANY OF THE FOREGOING SERIES.

Besides the compounds of various classes of which we have been speaking, there are others which are not included in these principal series. Among these bodies, some without doubt do belong to these series, but they are as yet so imperfectly known that the places they should occupy cannot at present be determined. With others, again, this is very doubtful, although possible, as in the case of the albuminoid substances, which, properly speaking, do not constitute chemical species; they are organs, or the remains of organs, whose history belongs to biology rather than to chemistry. We only speak of them here because it is usual to include them in works on chemistry.

These compounds may be divided into five groups:

1st. The natural alkaloids.

2nd. Uric acid and its derivatives.

3rd. Xanthine, hypoxanthine, guanine, creatine, etc., bodies which have all intimate relations to each other.

4th. Albuminoid principles.

5th. Gelatinous substances.

### NATURAL ALKALOIDS.

There are extracted from certain vegetables, bodies which can combine directly with acids to form salts, in the same manner as ammonia and the artificial organic alkalies. These bodies are called natural alkaloids, and may be divided into two classes.

The first class includes those which do not contain oxygen. They are volatile, and consequently are termed volatile natural alkaloids.

The second class contains those which are oxygenized, and are called fixed alkaloids, because the greater number of them cannot be reduced to vapour.[*]

### VOLATILE ALKALOIDS.

Extraction.—These alkaloids exist in vegetables, sometimes in the state of soluble and sometimes in that of insoluble salts. If they are in the former state, a concentrated decoction of the plant is made and an excess of potash is added to this solution, which is then shaken with ether. The alkaloid set free dissolves in this liquid, as do also some impurities. The ether is then saturated with a dilute acid, whereby a salt is formed which is soluble in water, but insoluble in ether, so that the impurities remain in this latter liquid, while the alkaloid passes into aqueous solution. On submitting this solution to the same treatment as the original decoction, an ethereal solution of the alkaloid is obtained: this is heated for some time at 100° in order to drive off the ether, and the residue is distilled.

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[*] The recent researches of Dr. Helwig prove that the natural alkaloids may be volatilized in minute quantities unchanged, and Dr. Guy, in a series of essays, has shown how this may be taken advantage of so as to detect even the $\frac{1}{10000}$ of a grain. For a summary of the results of his experiments, see the "Pharmaceutical Journal," October, 1867, page 197.—(Trs.)

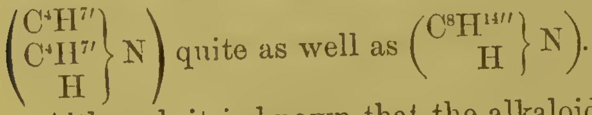
Nicotina is extracted from tobacco by this process.

The plant may also be distilled in presence of potash, the distilled product saturated by sulphuric acid, evaporated to dryness, and redissolved in alcohol, which takes up the salt of the alkaloid sought for, but not the sulphate of ammonium which is always mixed with it; the alkaloid may then be extracted from its sulphate as in the preceding process. Conia is extracted in this manner from the seeds of the hemlock.

If the alkaloids be in the state of insoluble salts, they should first be transformed into soluble salts by boiling the plants with dilute hydrochloric or sulphuric acid.

Properties.—The properties of these alkaloids are perfectly similar to those of the artificial alkaloids, with which they should be classed. One part of their hydrogen may be replaced by alcohol radicles. But, on introducing one or at most two alcohol radicles into the bodies of this class actually known, they are transformed into quaternary ammonias. These compounds are therefore either secondary or tertiary alkaloids. Thus, conia ($C^8H^{15}N$) is a secondary alkaloid $\left(\left.\begin{matrix}C^8H^{14}\\H\end{matrix}\right\}N\right)$.

As these bodies have never been produced synthetically, it is almost impossible to know whether the radicles there substituted for $H^2$ or $H^3$ constitute indivisible bi- or tri-atomic groups, or whether they constitute several different monatomic groups: conia may have for formula



$$\left(\left.\begin{matrix}C^4H^{7\prime}\\C^4H^{7\prime}\\H\end{matrix}\right\}N\right) \text{ quite as well as } \left(\left.\begin{matrix}C^8H^{14\prime\prime}\\H\end{matrix}\right\}N\right).$$

Although it is known that the alkaloids of which we speak have a constitution analogous to that of the compound ammonias, it is impossible at present to decide to which series they belong, and for this reason we have placed them among those bodies whose series have not been determined. These alkaloids are very active poisons.

One of the most important among them is nicotina, the alkaloid of tobacco.

Nicotina has the formula ($C^{10}H^{14}N^2$). It is a transparent, colourless, oleaginous liquid, having a slight odour of tobacco and a burning taste. Its density in the liquid state is 1·033 at 4°, and its vapour density is 5·607.

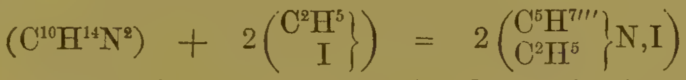
Nicotina gradually absorbs the oxygen of the air, becoming yellow and thick; it easily dissolves in water, alcohol, ether, and the essence of turpentine, and is very hygroscopic, absorbing as much as 177 per cent. of water when in a saturated atmosphere. Thus hydrated, it becomes solidified in a mixture of ice and salt. When dried over potash and anhydrous, it remains fluid at $-10°$.

It boils at about 250°, becoming slightly altered. The best method of obtaining it perfectly pure is to distil it with water or in vacuo. Its vapours are so irritating that respiration is exceedingly difficult in any room in which a single drop of this alkaloid has been volatilized.

Nicotina is lævogyrate; its aqueous solution is strongly alkaline, and precipitates a great number of metallic salts.

Iodine combines with this alkaloid, and gives a new alkaloid—iodo-nicotina ($C^{10}H^{14}N^{2}I^{6}$), which, like nicotina itself, can give crystallized salts. This iodo-nicotina is decomposed by heat, liberating iodine. Potash also separates the iodine from the nicotina.

Nicotina, derived from two molecules of ammonia, unites with two molecules of monatomic acids; its hydrochlorate is ($C^{10}H^{14}N^{2},2HCl$). Treated with hydriodic ethers, nicotina gives ethylated or methylated derivatives of the compound ammonium ($C^{5}H^{8}N$) = $\left(\left.\begin{matrix} C^{5}H^{7'''} \\ H \end{matrix}\right\} N\right)$.



$$(C^{10}H^{14}N^{2}) + 2\left(\left.\begin{matrix} C^{2}H^{5} \\ I \end{matrix}\right\}\right) = 2\left(\left.\begin{matrix} C^{5}H^{7'''} \\ C^{2}H^{5} \end{matrix}\right\} N,I\right)$$

Nicotina. Iodide of ethyl. Iodide of ethyl-nicotyl-ammonium.

This mode of action, quite unusual with the hydriodic ethers, tends to prove that nicotina contains the triatomic group ($C^{5}H^{7}$) twice; its formula, according to this, would be $\left(\left.\begin{matrix} C^{5}H^{7'''} \\ C^{5}H^{7'''} \end{matrix}\right\} N^{2}\right)$.

## FIXED ALKALOIDS.

Extraction.—The process of extraction differs a little, according to whether these bodies are soluble in water or not. When they are insoluble in this liquid, as is generally the case, a decoction of the plant is made, either with pure water if the salts contained in the plant are soluble, or with water acidulated by a mineral acid if the contrary be the case; then, after filtering and sufficiently concentrating the solution, it is precipitated by lime, ammonia, or carbonate of sodium. The precipitate is collected on a filter, washed and dried. It is then treated with alcohol, which dissolves the alkaloid, and the solution is filtered and evaporated. Sometimes it is useful to decolorize the alcoholic solution by animal charcoal. Often, also, the purification requires a series of operations which cannot be described here, because they vary in each particular case, but which are included in the general processes of proximate analysis which we have given elsewhere.

When the alkaloid is soluble in water, we obtain either a soluble sulphate or hydrochlorate by the different methods mentioned in the description of proximate analysis. When the hydrochlorate is obtained, the solution of this salt is treated with a slight excess of oxide of silver, and when it is the sulphate which is produced, the liquid is exactly neutralized by baryta water in order to remove the sulphuric acid.

In either case the alkaloid remains in solution in the water, and the liquid is filtered and evaporated.

Properties.—1st. A great number of these alkaloids possess very marked basic properties, and saturate the strongest acids. All are oxygenized.

2nd. Iodized iodide of potassium, the solution of the double iodide of potassium and mercury, the phospho-molybdate of sodium, and gallotannic acid, precipitate all the alkaloids without exception, even in dilute solution. The potassic iodide of mercury and the phospho-molybdate especially are very useful in an analytical point of view.

3rd. When distilled with potassic or sodic hydrate, fixed alkaloids are generally decomposed, and among the products of their decomposition volatile alkaloids are found. For instance, under these conditions cinchonine furnishes quinoline ($C^9H^7N$), lepidine ($C^{10}H^9N$), pyrridine ($C^{10}H^5N$), piccoline ($C^6H^7N$), lutidine ($C^7H^9N$), and collidine ($C^8H^{11}N$).

4th. When the iodide of ethyl or of methyl acts on these bodies, a direct addition takes place. The iodide thus formed, submitted to the action of moist oxide of silver, gives rise to a hydrate of quaternary ammonium.* All these bases should therefore be considered as tertiary. They are, moreover, sometimes monamines, sometimes diamines, etc.

5th. These alkaloids are generally very powerful poisons, or, at least, very active medicines.

Constitution of fixed Alkaloids.—For a long time the natural oxygenized alkaloids were compared to the ureas, that is to say, they were believed to be basic amides. This hypothesis can scarcely be admitted, at least for those whose basic properties are well marked. Basic amides, like ureas, are always very weak bases.

The natural oxygenized alkaloids should rather be considered as resembling the artificial oxygenized alkaloids discovered by M. Wurtz. The only point in which they differ is that they do not, like these latter, possess three replaceable atoms of hydrogen. This difference can, however, be very easily explained. The alkaloids of M. Wurtz would no longer possess replaceable hydrogen if alcohol radicles were substituted for those they contain: thus the hypothetical alkaloid which would probably be obtained by substituting three atoms of ethyl for three of hydrogen in trioxethylamine $\left[\left(\left.\begin{matrix}C^2H^{4''}\\H\end{matrix}\right\}O\right)'^{3}N\right]$, might properly be compared, from its properties and composition, to the natural oxygenized alkaloids:

---

* It is known that an alkaloid is at the fourth degree of substitution when the iodide of methyl produces no further substitution in it.

LEEDS SCHOOL OF MEDICINE

$$\left.\begin{array}{l} \left[\begin{array}{l} C^2H^{4''} \\ C^2H^5 \end{array}\right\} O\Big]' \\ \left[\begin{array}{l} C^2H^{4''} \\ C^2H^5 \end{array}\right\} O\Big]' \\ \left[\begin{array}{l} C^2H^{4''} \\ C^2H^5 \end{array}\right\} O\Big]' \end{array}\right\} N \quad = \quad C^{12}H^{27}NO^3$$

The following are the principal natural alkaloids:

### Alkalies from the Seeds of the Peganum Harmala.

| | |
|---|---|
| Harmaline | $C^{13}H^{14}N^2O$ |
| Harmine | $C^{13}H^{12}N^2O$ |

### Alkaloids from Opium.

| | |
|---|---|
| Morphia | $C^{17}H^{19}NO^3$,aq |
| Codeia | $C^{18}H^{21}NO^3$,aq |
| Thebaia | $C^{19}H^{31}NO^3$ |
| Papaverine | $C^{20}H^{21}NO^4$ |
| Narcotina | $C^{23}H^{25}NO^7$ |
| Narcein | $C^{23}H^{29}NO^9$ |

### Alkaloids from the Strychnos Tribe.

| | |
|---|---|
| Strychnia | $C^{21}H^{22}N^2O^2$ |
| Brucia | $C^{23}H^{26}N^2O^4$,4aq. |

### Alkaloids from the Cinchonas.

| | |
|---|---|
| Quina | $C^{20}H^{24}N^2O^2$,*n*aq. |
| Quinidine | |
| Quinicine | |
| Cinchonia | $C^{26}H^{24}N^2O$ |
| Cinchonidine | |
| Cinchonicine | |
| Aricine | $C^{23}H^{26}N^2O^4$ |

### The Alkaloid from Aconite.

| | |
|---|---|
| Aconitia | $C^{30}H^{47}NO^7$ |

### The Alkaloid from Veratrum Album.

| | |
|---|---|
| Veratria | $C^{32}H^{52}N^2O^8$ |

### The Alkaloid from Belladonna.

| | |
|---|---|
| Atropia | $C^{17}H^{23}NO^3$ |

## STUDY OF THE MOST IMPORTANT FIXED ALKALOIDS.

**Morphia** ($C^{17}H^{19}NO^3+2aq$).—In order to prepare morphia, opium is exhausted several times by lukewarm water, and pressed after each exhaustion. The liquids are then evaporated at 65° or 75° by means of a current of vapour, 100 grammes of powdered marble for each kilogramme of opium having first been added. When the liquid has acquired the consistence of syrup, water is added, the meconate of calcium deposited is separated by filtration, and the liquid is concentrated by a gentle heat. Then a solution consisting of 100 grammes of water, 50 grammes of chloride of calcium and 8 grammes of hydrochloric acid for each kilogramme of opium, is added to the hot concentrated liquid, and the mixture is left alone for 15 days. At the end of this time, the crystals of hydrochlorate of morphia which are deposited are expressed in a linen cloth, dissolved in alcohol, and again crystallized after their solution has been bleached by animal charcoal.

Morphia may be very easily prepared from this hydrochlorate by dissolving it in water and precipitating the solution by ammonia. But it is important that no more than the sufficient quantity of this reagent be employed or the morphia would be lost, as it is soluble in ammonia.

Genuine Smyrna opium contains from 10 to 15 per cent. of morphia.

In order to obtain perfectly pure morphia, it must be exhausted by ether, which has no action on morphia, but dissolves the small quantity of narcotina which it usually contains. Morphia crystallizes in transparent crystals of the fourth system. A thousand parts of cold water dissolve about one part of morphia; boiling water two, alcohol fifty, and ether scarcely any traces of it: fixed alkalies and ammonia readily dissolve it. Its solutions are very bitter, and are lævogyrate.

The crystals of morphia melt when heated, disengaging 5·94 per cent., that is to say, one molecule of water of crystallization; on cooling, the melted mass assumes a stellate appearance. If heated more strongly it becomes charred, emits an odour of resin, and even burns with a bright red flame. On contact with concentrated nitric acid, morphia assumes a beautiful red colour: its solution reduces iodic acid and precipitates iodine. In presence of morphia, chloride of gold assumes a blue shade; perchloride of iron also becomes blue, but this colour is extremely evanescent.

With morphia, iodine gives a compound called iodomorphia, whose formula appears to be $4(C^{17}H^{19}NO^3I^6)$.

Heated to 200° with caustic alkalies, morphia disengages methylamine.

The iodides of methyl and ethyl react on morphia when hot, and transform it into iodide of quaternary ammoniums which furnish the corresponding hydrates when submitted to the action of moist oxide of silver:

$$\underset{\text{Morphia.}}{(C^{17}H^{19}NO^{3})} + \underset{\text{Iodide of ethyl.}}{(C^{2}H^{5}I)} = \underset{\text{Iodide of morphyl-ethyl-ammonium.}}{(C^{17}H^{19}(C^{2}H^{5})NO^{3}.I)}$$

On treating morphia with dilute acids, salts are obtained which readily dissolve in water and in alcohol, are insoluble in ether, very bitter, and generally crystallizable.

With caustic alkalies and with ammonia these salts give a precipitate of morphia, soluble in an excess of the reagent: they are also precipitated by the general reagents of the alkaloids (tannic acid, iodized iodide of potassium, etc.).

In the action of oxidizing agents on morphia, a simple oxidation of this alkaloid appears to be produced. By treating a solution of the hydrochlorate of morphia with nitrate of silver at 60°, M. Schützenberger has obtained a disengagement of binoxide of nitrogen, and the deposition of the slightly soluble hydrochlorate of a new base, the formula of which is $(C^{17}H^{19}NO^{4})$; only differing therefore from morphia by containing one atom more of oxygen, and which for this reason M. Schützenberger calls *oxymorphia.*

On causing the nitrite of silver to act on a boiling concentrated solution of hydrochlorate of morphia, the same author has obtained a second base containing one molecule of water more than the preceding: its formula is $(C^{17}H^{21}NO^{5})$.

When one drop of a solution of a salt of morphia containing 1 per cent. of this substance is mixed with 10 or 15 drops of a solution of nitrate of silver of the strength of 1·77 per cent., after agitating for several minutes a beautiful precipitate of reduced silver is obtained. If the nitrate of silver have been previously heated in a porcelain capsule, the reduction of the metal is almost instantaneous, and the silver forms an adhesive layer on the capsule.

The salts of morphia chiefly used are the hydrochlorate, the acetate, and the sulphate.

The hydrochlorate dissolves in 20 parts of cold water: in the solid state it presents the appearance of silky tufts; its formula is $(C^{17}H^{19}NO^{3},HCl+3aq.)$.

The formula of the crystallized sulphate is $[(C^{17}H^{19}NO^{3})^{2}H^{2}SO^{4}+5\,aq.]$

The formula of the acetate is not accurately known. It is an instable salt which crystallizes with difficulty and which, when left alone, loses acetic acid.

Morphia is a powerful poison; its salts are used in medicine in doses of from $\frac{1}{8}$ to $\frac{1}{2}$ a grain.

Codeia $(C^{18}H^{21}NO^{3}+aq.)$.—In the preparation of morphia, the crystals of hydrochlorate which are obtained, and then decomposed by ammonia, contain small quantities of codeia. This alkaloid remains dissolved when the morphia is precipitated by ammonia. After separating the precipitate, the liquid is evaporated over a water-bath to remove the slight excess of ammonia, in order that all the morphia may be deposited. This new deposit is separated by filtration, the filtered liquid is concentrated and precipitated by caustic potash. The precipitate of codeia is washed, dried, and dissolved in ether, from which it is deposited in crystals. In order to obtain pure codeia, before crystallizing the precipitate must be redissolved in hydrochloric acid, its solution decolorized by animal charcoal and again precipitated.

Codeia takes the form of large octahedral crystals of the fourth system, containing one molecule of water of crystallization. It melts at 150° and decomposes at a higher temperature. This alkaloid dissolves in water more readily than morphia: 100 parts of water dissolve 1·26 parts at 15°, and 4 parts at 100°; it dissolves readily in alcohol and ether; this latter property distinguishes it from morphia.

Codeia is lævogyrate. Its solutions restore the blue colour to litmus reddened by acids.

It is not reddened by nitric acid, and does not assume a blue colour under the influence of ferric salts. It is employed in medicine as an anodyne in the same cases as morphia: its action appears less irritating.

The salts of codeia are almost all crystallizable, but they have not been much studied. With codeia, iodine gives a compound, iodocodeia, which has the formula ($C^{18}H^{21}NO^{3},I^{6}$) and which decomposes at 100°.

A concentrated alcoholic solution of codeia absorbs cyanogen, first assuming a yellow, then a brown colour. The liquid gradually deposits crystals of cyano-codeia ($C^{18}H^{21}NO^{3}.Cy^{2}$).

**Narcotina** ($C^{23}H^{25}NO^{7}$).—Narcotina is found in the cake of opium which remains under the press when this substance has been exhausted by water. In order to extract this alkaloid, the cake is treated with dilute hydrochloric acid which dissolves the narcotina, and the cake is again pressed. The acid solution is then precipitated by carbonate of sodium, and the dried precipitate is exhausted with boiling alcohol of 80 per cent. The alcoholic solution when suitably evaporated deposits crystals of narcotina, which are purified by a fresh crystallization, or if necessary by means of animal charcoal.

Narcotina crystallizes in right prisms having a rhombic base, or in flat, colourless, transparent brilliant needles grouped in bundles. It is insoluble in cold water, and boiling water only dissolves $\frac{1}{7000}$; it is very slightly soluble in ether or alcohol. Its solutions are bitter, and do not restore the blue colour of reddened litmus.

Narcotina is strongly lævogyrate; acids modify this rotatory power considerably and change its direction.

Neither ammonia nor potash dissolves narcotina, and ferric salts do not assume a blue colour under its influence.

At 170° narcotina melts into a liquid which crystallizes when cooled slowly, but when rapidly cooled becomes an amorphous mass; a little above its fusing point it becomes coloured; at 220° it swells out, disengages ammonia, and leaves humopic acid; heated to 200° in a closed tube with water, it dissolves, giving a very bitter reddish-yellow liquid.

When distilled with potash, narcotina furnishes a volatile alkaloid, which, according to Wertheim, is tritylamine (propylamine), or perhaps its isomer trimethylamine.

Under the influence of oxidizing agents, narcotina gives a number of products which the scope of this work does not permit us to study.

Narcotina acts less powerfully than morphia on the animal economy; it is, however, sufficiently poisonous to kill a dog when administered in a dose of a gramme and a half (23 grains).

As the basic properties of narcotina are very feeble, its salts formed by combination with acids have very little stability. These salts decompose when their solutions are evaporated, and sometimes even when they are diluted, The sub-acetate of lead precipitates their narcotina, which distinguishes this body from the greater number of the other organic alkaloids.

**Strychnia** ($C^{21}H^{22}N^{2}O^{2}$).—This body is extracted from the bean of the strychnos Ignatii, and from nux vomica, in which it is found mixed with brucia, and which, though it contains less than the St. Ignatius's bean, is much cheaper, and is therefore employed exclusively in the preparation of this alkaloid.

The nux vomica beans are reduced to powder, exhausted with very dilute boiling sulphuric acid, and pressed. The acid liquid is then saturated by an excess of hydrate of calcium. There is thus formed a precipitate of calcic sulphate, strychnia, and brucia, which is collected on a filter, pressed, dried, and acted upon by boiling alcohol, which dissolves the strychnia and brucia. This solution is filtered while hot; and on cooling the greater part of the strychnia is deposited from the alcohol in a crystallized state, while the brucia remains in solution, and may be obtained by the evaporation of the liquid. These two alkaloids are then purified by repeated crystallizations from alcohol.

Strychnia crystallizes in octahedra having a rectangular base, or in quadrilateral prisms terminated by pyramids having four faces. It is colourless, inodorous, intensely bitter, and leaves a disagreeable after-taste.

One part of strychnia requires 6667 parts of water at 10° for its solution, and 2500 parts of boiling water. Ordinary alcohol dissolves it pretty freely, absolute alcohol very slightly, and ether not at all: the essential oils dissolve it readily.

Strychnia in alcoholic solution is strongly levogyrate, but this rotatory power is modified by acids. Distilled with caustic potash, strychnia furnishes a volatile alkaloid whose formula is ($C^{9}H^{7}N$), and which is known as quinoline. When mixed with binoxide of lead or bichromate of potassium, and then moistened with sulphuric acid, strychnia assumes a beautiful blue colour, which quickly becomes violet, then red, and finally pure yellow.

Concentrated nitric acid does not impart a red colour to strychnia; at most it only turns it yellow.

Strychnia is one of the most powerful poisons known: five centigrammes ($\frac{3}{4}$ grain) of this body kill a man in a quarter of an hour, producing violent attacks of tetanus. According to M. Vella, woorara injected into the blood is the best antidote for strychnia: under its influence, the symptoms of poisoning suddenly cease. This property, possessed by woorara, is not owing to any chemical combination taking place between it and strychnia, but to its action on the animal economy, which is the reverse of that of strychnia.

Under the influence of chlorine, strychnia gives products of substitution which retain all the poisonous properties of this alkaloid. Iodine converts it into iodostrychnia $[(C^{21}H^{22}N^2O^2)^4,I^6]$.

Submitted to the influence of iodide of methyl, strychnia gives a new alkaloid, which is derived by the substitution of one atom of methyl for an atom of hydrogen. This body is not poisonous.

The salts of strychnia are very bitter: the carbonate of sodium and the caustic alkalies added to their solutions give rise to precipitates which are insoluble in an excess of the reagent. Ammonia causes the formation of a precipitate which an excess of the reagent redissolves, but which again precipitates after a certain time, and does not afterwards dissolve, whatever may be the quantity of ammonia added.

Strychnia is used in paralysis. Its sulphate has been unsuccessfully tried in cholera.

**Brucia** ($C^{23}H^{26}N^2O^4$ + 4 aq.).—We have already seen how this alkaloid is extracted from the vegetables which contain it; the following are its properties:

Brucia crystallizes in right rhombic prisms. It is very slightly soluble in water, but rather more so than strychnia; it is very soluble in alcohol, and insoluble in ether. Its solutions are lævogyrate, but acids weaken its rotatory power.

The crystals of brucia contain four molecules of water of crystallization, which they lose by efflorescence.

Concentrated sulphuric acid imparts first a rose colour, then a yellow, and finally a yellowish-green colour to brucia. Concentrated nitric acid turns it a beautiful red colour; and, according to Gerhardt, nitrate of methyl is disengaged in this reaction.

Distilled with sulphuric acid and peroxide of manganese, this alkaloid gives, amongst other products, formic acid and an inflammable liquid, which appears to be methylic alcohol.

With iodine, brucia gives two special compounds; the formula of one is $[(C^{23}H^{26}N^2O^4)^2,I^6]$, and that of the other $[(C^{23}H^{26}N^2O^4)^4,I^6]$.

With chlorine and bromine, brucia gives products of substitution.

The salts of brucia have a bitter taste, and most of them crystallize: nitric acid colours them red like brucia itself.

They are decomposed by fixed alkalies, which precipitate brucia from their solutions. Ammonia also precipitates brucia. This is dissolved in an excess of the reagent, but is deposited after a time, and then will not again dissolve in ammonia.

Strychnia and morphia displace brucia from its salts.

Aqueous solutions of these salts mixed with a slight excess of tartaric acid do not become cloudy by the addition of alkaline bicarbonates.

**Quina** ($C^{20}H^{24}N^{2}O^{2}$) + *n* aq.—Quina is found in the different species of cinchonas, where it is mixed with cinchonia. The yellow cinchona contains the greatest quantity of it; but as it is very expensive, a species of cinchona of an inferior quality imported from Australia is largely used in the manufacture of the sulphate of quina.

In order to extract quina from cinchona, the latter is reduced to powder, then boiled several times with dilute hydrochloric or sulphuric acid, the cinchona being pressed after each boiling. When it is exhausted, the liquids are mixed and precipitated by carbonate of sodium: quina, cinchonia, and several impurities separate from the liquids; this deposit is collected on a linen cloth, pressed, dried, and exhausted by alcohol of 85 or 90 per cent.

This solution is treated by a quantity of dilute sulphuric acid just sufficient to saturate the alkaloids, after which the alcohol is removed by distillation: on cooling, the sulphate of quina crystallizes, while the sulphate of cinchonia, which is much more soluble, remains in solution. The crystals are separated by straining, and are purified by repeated crystallizations, the solutions being treated with animal charcoal.

The mother-liquor still containing quina, it is precipitated by carbonate of sodium, the precipitate is again dissolved in sulphuric acid, and the sulphate of quina is separated by fresh crystallizations.

Of late years this process has been slightly modified. Instead of exhausting the cinchona by an acid, precipitating by alkaline carbonate and redissolving the precipitate by alcohol, an alcoholic solution is obtained directly.

To effect this, the powdered cinchona is mixed with lime, and then exhausted by alcohol. The lime seizes the quinic acid and tannin of the cinchona (red cinchonic) with which the alkaloids are combined, and these set free are dissolved in the alcohol.

The pure sulphate of quina is extracted from this alcoholic solution as in the preceding process.

Pure quina may be obtained by precipitation from its sulphate by a mineral alkali.

Quina thus prepared is a white amorphous mass. It is inodorous, very bitter, soluble in about 350 parts of cold and 400 parts of boiling water, in 2 parts of cold alcohol, 60 parts of ether, and 6 parts of chloroform. The fatty and essential oils also dissolve it. Its alcoholic solution is lævogyrate, but this rotatory power diminishes as the temperature increases, and augments under the influence of acids.

Quina is a powerful alkaloid: it restores the blue colour to litmus paper reddened by acids; with most acids it gives well-defined salts, and dissolves in water containing carbonic anhydride, forming a soluble carbonate.

When a dilute solution of sulphate of quina is precipitated by excess of ammonia, and the mixture left for some time, fine needles form which contain three molecules of water of crystallization: this hydrate, like pure quina, is not deposited in crystals from its solution in alcohol.

Another hydrate, only containing one molecule of water, is obtained by leaving quina recently precipitated for a long time in contact with air, care being taken to keep it moist: this second hydrate may be recrystallized from alcohol.

Dilute acids readily dissolve quina. These solutions are strongly dichroic, that is to say, they present a blue colour when interposed between the eye and the light.

Concentrated sulphuric acid and nitric acid dissolve quina when cold without colouring it; when hot, the solution obtained by means of sulphuric acid turns red, and then black.

When chlorinated water and a few drops of ammonia are added to the solution of a salt of quina, a green colour is produced. This colour becomes violet, and then deep red, by a further addition of chlorinated water, if care have been taken not to employ an excess of ammonia.

When chlorinated water, concentrated and free from hydrochloric acid, is poured into a solution of sulphate of quina, and powdered ferrocyanide of potassium is added, the liquid soon assumes a deep-red colour: the same colour is produced when lime water, or baryta water, or sodic phosphate or borate are substituted for the potassic ferrocyanide.

When rubbed up with iodine, quina gives a brown matter; the same probably as is precipitated when the solution of a salt of quina is treated by iodized iodide of potassium. The formula $[(C^{20}H^{24}N^2O^2)^2,I^2]$ has been attributed to this substance.

A sulphate of iodo-quina $(C^{20}H^{24}N^2O^2I^2H^2SO^4)$ is obtained by adding an alcoholic solution of iodine to a hot concentrated solution of the neutral sulphate of quina in strong acetic acid; large well-crystallized plates of sulphate of iodo-quina are deposited after several hours. This salt possesses the same optical properties as tourmaline, and might be substituted for this latter body in the construction of apparatus for the polarization of light.

When quina is distilled with hydrate of potassium, quinoline, or rather a mixture of quinoline, lepidine, pyrridine, piccoline, lutidine, and collidine is produced.

The iodides of ethyl or of methyl combine with quina, forming iodides corresponding to the alkaloids which, in a free state, are derived from the hydrate of ammonium type:

$$\underset{\text{Quinine.}}{(C^{20}H^{24}N^2O^2)} + \underset{\text{Iodide of ethyl.}}{(C^2H^5I)} = \underset{\text{Iodide of ethyl-quinyl-ammonium.}}{(C^{20}H^{24}N^2O^2.C^2H^5.I)}$$

These iodides are transformed into corresponding hydrates by moist oxide of silver: the hydrates possess very marked basic properties.

Quina and its salts are very powerful febrifuges.

Derived from two molecules of ammonia, quina is biatomic and biacid; it can unite with a molecule of a monatomic acid in order to form a basic salt, or with two molecules of the same acid to form a neutral salt:

$C^{20}H^{24}N^2O^2,HCl+3aq.$ . . . . . basic hydrochlorate.
$C^{20}H^{24}N^2O^2,2HCl$ . . . . . . neutral hydrochlorate.

Its tendencies are however rather monoacid; the basic salts are much more stable than the biacid salts.

Quina also forms two sulphates; one, the sulphate of commerce, is basic, contains two molecules of quina for one of sulphuric acid, and has for formula $[(C^{20}H^{24}N^2O^2)^2,H^2SO^4+7aq.]$, and the other is neutral and is produced when a quantity of sulphuric acid equal to that it already contains is added to the preceding sulphate. The formula of this latter is $[C^{20}H^{24}N^2O^2,H^2SO^4+7aq.]$; it is much more soluble than the basic sulphate, and it is well in pharmaceutic preparations containing this latter salt to add a little sulphuric acid in order to dissolve it.

Many authors consider the salt we call basic as neutral, and that we call neutral as acid. But quina being a diamine, the nomenclature we have adopted appears to us to be preferable.

The sulphate of quina being a valuable medicine, and at the same time very expensive, it is often adulterated. The substances used for this purpose are crystallized sulphate of calcium, boracic acid, mannite, sugar, starch, salicin, stearic acid, and the sulphates of cinchonia and quinidine. These different adulterations may be discovered by the following methods:

1st. By gently heating the sulphate of quina with alcohol to 21° (2 gr. of the salt to 120 gr. of alcohol), it completely dissolves: an insoluble residue, on the contrary, is left if it be mixed with starch, magnesia, mineral salts, or certain other foreign substances.

2nd. Mineral substances which are capable of dissolving in alcohol may be discovered by incinerating the salt suspected. These substances remain as residue, while pure sulphate of quina should not leave any ash.

3rd. Salicin may be known by the deep-red colour that salt assumes on contact with concentrated sulphuric acid.

4th. Stearic acid remains as residue when the sulphate of quina is dissolved in acidulated water.

5th. In order to discover sugar and mannite,.the salt is dissolved in acidulated water, and its solution precipitated by a slight excess of barytic hydrate: a deposit of quina and barytic sulphate is formed. A current of carbonic anhydride is transmitted through the liquid to remove the excess of barium in the state of insoluble carbonate; then it is boiled in order to precipitate the quina which may have been dissolved by means of the carbonic anhydride, and it is finally filtered. If the sulphate examined be pure, the filtered liquid should not leave any perceptible residue when evaporated: it would leave one, on the contrary, if this salt contained sugar or mannite.

6th. The sulphate of quina always contains 2 or 3 per cent. of sulphate of cinchonia, arising, not from adulteration, but from incomplete purification.

The best method of determining the respective quantities of quina and cinchonia contained in the sulphate examined is the following:

A few grammes of ammonia and ether washed with water are added to one or two grammes of the salt; they are well shaken together and then left to rest. An ethereal solution containing all the quina floats on the surface, while the cinchonia, being but little soluble in water or ether, remains in suspension in a lower aqueous stratum. The ether is separated by means of a funnel with a stopcock, evaporated, and the residue it leaves is weighed. The same operation is repeated, chloroform being now substituted for the ether, as it dissolves both the quina and the cinchonia. When this liquid is evaporated, a residue is left which is heavier than the first. The difference between the weights of the two residues gives the weight of the cinchonia.

7th. In order to detect the sulphate of quinidine, the great difference in solubility between the oxalates of quina and quinidine is made use of. The oxalate of quinidine is so soluble in cold water that it is not precipitated in the double decomposition produced when solutions of oxalate of ammonium and sulphate of quinidine are mixed. Under the same conditions, quina, on the contrary, is precipitated so that the liquid only retains slight traces of it. The operation is conducted in the following manner:

Ten grammes of the suspected salt are dissolved in water, precipitated by a slight excess of oxalate of ammonia and filtered. If the sulphate be pure, the filtered liquid scarcely becomes cloudy by the addition of ammonium; if, on the contrary, it contain sulphate of quinidine, this latter is wholly contained in the filtered liquid, which gives an abundant precipitate when ammonia is added.

**Cinchonia** ($C^{20}H^{24}N^{2}O$).—It has been seen that the mother-liquors obtained in the preparation of sulphate of quina contain also sulphate of cinchonia. This latter alkaloid may be extracted in a pure state by precipitating by sodic carbonate and digesting the precipitate in ether, which dissolves the quina and leaves the cinchonia. This latter is then dissolved in alcohol, the solution is decolorized by animal charcoal, filtered and left to evaporate slowly. The cinchonia is deposited crystallized in quadrilateral prisms or in fine colourless and brilliant needles, which do not contain any water of crystallization.

Cinchonia is insoluble in cold water, and requires 2500 parts of boiling water for its solution; it dissolves in alcohol less readily than does quina, and is almost insoluble in ether; it is slightly soluble in chloroform, and in the fatty and the essential oils. It has a bitter taste, which is developed slowly in consequence of the slight solubility of the alkaloid.

Solution of cinchonia possesses an alkaline reaction and is dextrogyrate. Its rotatory power is weakened by acids.

Cinchonia melts at 165° into a liquid which, on cooling, becomes a crystalline mass. At a higher temperature it is sublimed, emitting an aromatic odour. In hydrogen and ammoniacal gases cinchonia may be sublimed in the form of brilliant prisms nearly an inch in length.

Cinchonia presents considerable resistance to the action of oxidizing agents; it dissolves readily in acids, giving well-defined salts.

With chlorine or bromine it gives a chlorinated or brominated alkaloid. The solutions of its salts do not turn green, like those of quina, when ether, chlorine water, and ammonia are successively made to act upon them.

It acts in the same manner as quina with iodine and iodized iodide of potassium.

Distilled with the hydrate of potassium, it gives, like quina, a mixture of volatile alkaloids containing quinoline ($C^9H^7N$), lepidine ($C^{10}H^9N$), pyrridine ($C^{10}H^5N$), piccoline ($C^6H^7N$), lutidine ($C^7H^9N$), and collidine ($C^8H^{11}N$).

Cinchonia is less efficacious as a febrifuge than quina.

Its salts are generally more soluble in water and alcohol than those of quina.

Like quina, cinchonia forms two salts with each acid; one is neutral, and contains two molecules of a monatomic acid, or one molecule of a biatomic acid for each molecule of cinchonia; the other is basic, and contains a single molecule of a monatomic acid for one of cinchonia, or one molecule of a biatomic acid for two of cinchonia. For example:

| | |
|---|---|
| Basic hydrochlorate . . . | $C^{20}H^{24}N^2O.HCl$ |
| Neutral hydrochlorate . . | $C^{20}H^{24}N^2O.(HCl)^2$ |
| Basic sulphate . . . . . . | $(C^{20}H^{24}N^2O)^2.H^2SO^4+3aq.$ |
| Neutral sulphate . . . . | $C^{20}H^{24}N^2O.H^2SO^4+2aq.$ |

Cinchonia acts like quina with the iodide of methyl; with such bodies it forms iodides of alkaloids which, in a free state, belong to the type of hydrate of ammonium, and whose hydrates are obtained by causing moist oxide of silver to act on these iodides:

$$\underset{\text{Cinchonia.}}{(C^{20}H^{24}N^2O)} + \underset{\text{Iodide of methyl.}}{(CH^3I)} = \underset{\text{Iodide of methyl-cinchonyl-ammonium.}}{(C^{20}H^{24}(CH^3)N^2O.I)}$$

**Aconitina** ($C^{30}H^{47}NO^7$).—This alkaloid exists in the leaves of the *Aconitum napellus.* To extract it, these leaves are exhausted by alcohol, and the alcoholic solution is treated with hydrate of calcium. The alkaloid liberated by this base remains dissolved. The solution is filtered and sulphuric acid added. Sulphate of calcium is deposited, and separated by filtration; then the solution is evaporated to remove the alcohol, and the aconitina is precipitated in a more or less impure state from the aqueous solution by means of an alkaline carbonate. The precipitate is redissolved in alcohol, which is evaporated after having been decolorized by animal charcoal. The residue is redissolved in sulphuric acid, and again precipitated by an alkaline carbonate: this precipitate, treated with ether, leaves pure aconitina in solution.

In a pure state, aconitina is deposited from its solution in dilute alcohol in the form of white pulverulent grains, and sometimes also in the state of a compact vitreous transparent mass. It is inodorous, and very bitter, slightly soluble in cold water, and more so in boiling water, of which it requires 50 parts for its solution; this solution is strongly alkaline. It dissolves readily in alcohol, but is not soluble in ether. It is not coloured by the action of nitric acid, but sulphuric acid imparts first a yellow, then a violet-red colour to it.

Aconitina melts at 80°, and, on cooling, becomes a vitreous mass, without losing water; at 220° it becomes brown, and decomposes at a higher temperature.

With aconitina, tincture of iodine gives a precipitate of the colour of kermes.

Aconitina is a powerful poison, one milligramme of which will kill a bird in a few minutes, and five milligrammes will kill it immediately. The animal dies with violent tetanic convulsions. It also produces dilatation of the pupils.

The salts of aconitina crystallize with difficulty; they dissolve readily in alcohol and in water, but are not deliquescent. The alkalies precipitate aconitina from the aqueous solution of its salts.

**Veratria** ($C^{32}H^{52}N^{2}O^{8}$).—Veratria is found in the fruit of *Veratrum sabadilla*, in white hellebore (*Veratrum album*), and probably in other species of veratrum. It is extracted from the fruit of the Veratrum sabadilla, which has the husks removed and is powdered, by a similar process to that by which aconitina is extracted from *Aconitum napellus.*

Veratria is generally found in a white or greenish-white crystalline powder. It crystallizes in long prisms having a rhombic base by the spontaneous evaporation of its alcoholic solution. It is insoluble in water, and in alkaline liquids, very soluble in alcohol, and slightly so in ether. Its solutions turn litmus blue.

Veratria melts by heat, and is decomposed at a high temperature. Concentrated nitric acid colours it a beautiful scarlet, which afterwards becomes yellow; sulphuric acid colours it yellow, then reddish blue; concentrated hydrochloric acid dissolves it, giving, especially when hot, a deep-violet liquid.

Veratria dissolves in dilute acids. On evaporating these solutions, salts are obtained, of which many are crystallizable. Fixed alkalies and ammonia precipitate veratria from solutions of its salts.

Veratria is a powerful sternutatory, and is so poisonous that three milligrammes have killed a cat in ten minutes: when administered in small doses it causes vomiting and purging.

**Atropia** ($C^{17}H^{23}NO^{3}$).—Atropia is contained in belladonna (*Atropa belladonna*), and in the roots of the *Datura stramonium.*

To extract atropia from belladonna the roots of this plant are digested in alcohol, hydrate of calcium is added to this tincture to liberate the alkaloid, and the mixture is then filtered. The filtered liquid is saturated by a slight excess of dilute sulphuric acid, then boiled, to drive off the alcohol it contains, and finally precipitated by carbonate of potassium. As soon as it begins to turn cloudy it is filtered, and the atropia crystallizes after a little time. It is purified by several crystallizations from alcohol. The temperature must not be too high during this process, as atropia is easily decomposed.

Atropia crystallizes in tufts of silky needles; it is little soluble in water, more so in ether, and very soluble in alcohol. It is strongly alkaline, and has a very bitter taste; it melts at 90°, and is volatilized at 140° with partial decomposition.

Atropia dissolves readily in acids; its salts crystallize with difficulty, and are speedily decomposed in the air.

Chloric acid dissolves it, but again leaves it by spontaneous evaporation. Nitric acid attacks it, disengaging reddish vapours.

When atropia is boiled for some time with concentrated hydrochloric acid, an oil is formed which floats on the surface, and on cooling becomes a crystalline mass: the body thus produced possesses acid properties. The hydrochloric acid holds in solution an alkaloid whose formula is $(C^8H^{15}NO)$. This alkaloid is crystallizable, and melts at 60°. Atropia has been split up into *atropic acid* and an alkaloid, *tropine*, by submitting it to the action of hydrate of barium. M. Kraut, to whom we owe this experiment, has lately shown that the products obtained by barium are identical with those obtained by means of hydrochloric acid.

The composition of atropic acid now appears to be definitely settled. This acid is an isomer of cinnamic acid, and has the formula $(C^9H^8O^2)$. It is true that those who prepared it by means of hydrochloric acid wrote it $(C^{24}H^{22}O^5)$, but this is owing to the fact that it is difficult to obtain it pure by this method.

Atropic acid is always accompanied, according to M. Lossen's recent researches, by another acid, which contains an additional molecule of water, tropic acid $(C^9H^{10}O^3)$. The formation of these products is explained by the following equations:

$$\text{1st.}\quad \underset{\text{Atropia.}}{(C^{17}H^{23}NO^3)} + \underset{\text{Water.}}{(H^2O)} = \underset{\text{Tropic acid.}}{(C^9H^{10}O^3)} + \underset{\text{Tropine.}}{(C^8H^{15}NO)}$$

$$\text{2nd.}\quad \underset{\text{Tropic acid.}}{(C^9H^{10}O^3)} - \underset{\text{Water.}}{H^2O} = \underset{\text{Atropic acid.}}{(C^9H^8O^2)}$$

When a mixture of atropia and iodide of ethyl is heated, a crystalline precipitate is formed of iodide of ethyl-atropinium $(C^{17}H^{23}(C^2H^5)NO^3I)$.

Atropia acts as a violent poison on the animal economy. It dilates the pupil powerfully, imparts a dry sensation to the mouth, with constriction of the throat, and causes headache.

The salts of atropia are only precipitated by the alkalies when their solutions are highly concentrated; tannin only precipitates them in presence of hydrochloric acid.

## URIC ACID GROUP.

The fundamental compound of this group is uric acid ($C^5H^4N^4O^3$). This acid exists in the urine of carnivorous animals; herbivorous animals do not produce any unless they are kept from food, in which case they live at the expense of their own substance, that is to say, are brought to the condition of carnivorous animals.

When uric acid is submitted to oxidizing actions, it splits up into urea and alloxan:

$$\underset{\text{Uric acid.}}{(C^5H^4N^4O^3)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Oxygen.}}{O} = \underset{\text{Alloxan.}}{(C^4H^2N^2O^4)} + \underset{\text{Urea.}}{(CH^4N^2O)}$$

If alloxan be acted upon by bases it combines with them; but when we try to separate it from these combinations, alloxanic acid ($C^5H^4N^2O^5$) is obtained:

$$\underset{\text{Alloxan.}}{(C^4H^2N^2O^4)} + \underset{\text{Water.}}{(H^2O)} = \underset{\text{Alloxanic acid.}}{(C^4H^4N^2O^5)}$$

When alloxanates are boiled, they are transformed into mesoxalates and urea:

$$\underset{\text{Barytic alloxanate.}}{(C^4H^2Ba''N^2O^5)} + \underset{\text{Water.}}{(H^2O)} = \underset{\text{Barytic mesoxalate.}}{(C^3Ba''O^5)} + \underset{\text{Urea.}}{(CH^4N^2O)}$$

Submitted to the influence of reducing agents, alloxan fixes a molecule of hydrogen and is converted into dialuric acid:

$$\underset{\text{Alloxan.}}{(C^4H^2N^2O^4)} + \underset{\text{Hydrogen.}}{H^2} = \underset{\text{Dialuric acid.}}{(C^4H^4N^2O^4)}$$

If the reducing action be less prolonged, a compound of dialuric acid and alloxan is obtained, which results from the condensation of two molecules of alloxan into one, with fixation of $H^2$: this body is called alloxantin:

$$\underset{\text{Alloxan.}}{2(C^4H^2N^2O^4)} + \underset{\text{Hydrogen.}}{H^2} = \underset{\text{Alloxantin.}}{(C^8H^6N^4O^8)}$$

On mixing nine parts of dialuric acid with five of glycerine dried at 160°, and submitting the mixture for some time to a temperature of 140° or 150°, a solid mass is obtained which, when freed by water from the glycerine it contains, is the ammoniacal salt of a new acid, hydurilic acid. This salt, dissolved in boiling ammonia and precipitated when hot by sulphate of copper, gives a deposit of cupric hydurilate, from which the hydurilic acid may be extracted by means of hydrochloric acid:

$$\underset{\text{Dialuric acid.}}{5(C^4H^4N^2O^4)} = \underset{\text{Hydurilate of ammonium.}}{2(C^8H^5(NH^4)N^4O^6)} + \underset{\text{Carbonic anhydride.}}{3(CO^2)} + \underset{\text{Formic acid.}}{(CH^2O^2)}$$

Heated with nitric acid, hydurilic acid furnishes the following derivatives:

| | |
|---|---|
| Violuric (nitroso-barbituric) acid . . . . | $C^4H^3(NO)N^2O^3$. |
| Dilituric (nitro-barbituric) acid . . . . . | $C^4H^3(NO^2)N^2O^3$. |
| Violantin (a combination of the two preceding). | $C^8H^6(NO,NO^2)N^4O^6$. |

$$\underset{\text{Hydurilic acid.}}{(C^8H^6N^4O^6)} + \underset{\text{Nitric acid.}}{(NHO^3)} = \underset{\text{Violuric acid.}}{(C^4H^3(NO)N^2O^3)}$$

$$+ \underset{\text{Alloxan.}}{(C^4H^2N^2O^4)} + \underset{\text{Water.}}{(H^2O)}$$

$$\underset{\text{Hydurilic acid.}}{(C^8H^6N^4O^6)} + \underset{\text{Nitric acid.}}{2(NHO^3)} = \underset{\text{Dilituric acid.}}{(C^4H^3(NO^2)N^2O^3)} + \underset{\text{Alloxan.}}{(C^4H^2N^2O^4)}$$

$$+ \underset{\text{Nitrous acid.}}{(NHO^2)} + \underset{\text{Water.}}{(H^2O)}$$

Violuric and dilituric acids, when treated with bromine, lose the nitrogenized group they contain and an atom of hydrogen, and take in exchange a molecule of bromine; bibromo-barbituric acid is thus formed:

$$\underset{\text{Violuric acid.}}{(C^4H^3(NO)N^2O^3)} + \underset{\text{Bromine.}}{2\left(\left.\begin{matrix}Br\\Br\end{matrix}\right\}\right)} = \underset{\text{Nitrous bromide.}}{(NOBr)} + \underset{\text{Hydrobromic acid.}}{(HBr)}$$

$$+ \underset{\text{Bibromo-barbituric acid.}}{(C^4H^2Br^2N^2O^3)}$$

Under the action of reducing agents bibromo-barbituric acid can furnish monobromo-barbituric acid ($C^4H^3BrN^2O^3$) and barbituric acid ($C^4H^4N^2O^3$); when water intervenes in the reaction, it may be transformed into hydurilic and dialuric acids.

Dialuric acid ($C^4H^4N^2O^4$) is simply oxybarbituric acid:

$$\underset{\text{Barbituric acid.}}{(C^4H^4N^2O^3)} + \underset{\text{Oxygen.}}{O} = \underset{\text{Dialuric acid.}}{(C^4H^4N^2O^4)}$$

When barbituric acid is heated for some time, it is converted into dibarbituric acid, a molecule of water being eliminated:

$$\underset{\text{Barbituric acid.}}{2(C^4H^4N^2O^3)} = \underset{\text{Water.}}{(H^2O)} + \underset{\text{Dibarbituric acid.}}{(C^8H^6N^4O^5)}$$

Thus, starting from alloxan, the first product of oxidation of uric acid, the following series of compounds are obtained:

Alloxan . . . . . . . . . ($C^4H^2N^2O^4$)
Alloxanic acid . . . . . . . ($C^4H^4N^2O^5$) = a molecule of alloxan, plus a molecule of water.

Mesoxalic acid . . . . . . . ($C^3H^2O^5$)
Dialuric acid . . . . . . . . ($C^4H^4N^2O^4$) = a molecule of alloxan, plus a molecule of hydrogen.

Alloxantin ($C^8H^6N^4O^8$) = two molecules of alloxan, plus a molecule of hydrogen (a molecule of alloxan, plus one of dialuric acid).

Hydurilic acid ($C^8H^6N^4O^6$) = two molecules of dialuric acid, less an atom of oxygen and a molecule of water.

Barbituric acid ($C^4H^4N^2O^3$) = dialuric acid, less an atom of oxygen.

Lastly, the brominated, nitrogenized, nitrous, and nitroso-nitrogenized derivatives of barbituric acid:

| | |
|---|---|
| Bromo-barbituric acid . . . . . . . | $C^4H^3BrN^2O^3$ |
| Bibromo-barbituric acid . . . . . | $C^4H^2Br^2N^2O^3$ |
| Nitroso-barbituric (violuric) acid . . | $C^4H^3(NO)N^2O^3$ |
| Nitro-barbituric (dilituric) acid . . . | $C^4H^3(NO^2)N^2O^3$ |
| Violantin . . . . . . . . . . . . | $C^8H^6(NO,NO^2)N^4O^6$ |

A second group may be placed beside this first one. If alloxan be oxidized by means of nitric acid, carbon and oxygen are eliminated and parabanic acid ($C^3H^2N^2O^3$) is produced:

$$\underset{\text{Alloxan.}}{(C^4H^2N^2O^4)} + \underset{\text{Oxygen.}}{\Theta} = \underset{\substack{\text{Carbonic}\\ \text{anhydride.}}}{(CO^2)} + \underset{\text{Parabanic acid.}}{(C^3H^2N^2O^3)}$$

If parabanic acid be treated with ammonia, the ammoniacal salt of a new acid, oxaluric acid, is formed: this new acid bears the same relation to parabanic acid that alloxanic acid does to alloxan, that is to say, it contains a molecule more of water:

$$\underset{\text{Parabanic acid.}}{(C^3H^2N^2O^3)} + \underset{\text{Water.}}{(H^2O)} = \underset{\text{Oxaluric acid.}}{(C^3H^4N^2O^4)}$$

The aqueous solution of oxaluric acid is decomposed by heat into oxalic acid and urea:

$$\underset{\text{Oxaluric acid.}}{(C^3H^4N^2O^4)} + \underset{\text{Water.}}{(H^2O)} = \underset{\text{Oxalic acid.}}{(C^2H^2O^4)} + \underset{\text{Urea.}}{(CH^4N^2O)}$$

Under the influence of nascent hydrogen, parabanic acid becomes doubled and hydrogenized in the same manner as alloxan. Oxalantin is thereby produced:

$$\underset{\text{Parabanic acid.}}{2(C^3H^2N^2O^3)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}} = \underset{\text{Oxalantin.}}{(C^6H^6N^4O^6)}$$

Oxalantin appears to be identical with leucoturic acid, which is produced when alloxanic acid is decomposed by heat. In this reaction, allanturic acid ($C^3H^4N^2O^3$) is also produced, which differs from parabanic acid by containing $H^2$ more, exactly as dialuric acid differs by $+ H^2$ from alloxan:

$$\underset{\text{Parabanic acid.}}{(C^3H^2N^2O^3)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}} = \underset{\text{Allanturic acid.}}{(C^3H^4N^2O^3)}$$

The same reaction gives rise to hydantoin ($C^3H^4N^2O^2$), which represents allanturic acid less an atom of oxygen, and which consequently is to allanturic acid what barbituric is to dialuric acid:

$$\underset{\text{Allanturic acid.}}{(C^3H^4N^2O^3)} - \underset{\text{Oxygen.}}{O} = \underset{\text{Hydantoin.}}{(C^3H^4N^2O^2)}$$

The formation of these different products in the decomposition of alloxanic acid may be readily understood; there is first:

$$\underset{\text{Alloxanic acid.}}{(C^4H^4N^2O^5)} = \underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{CO^2} + \underset{\text{Hydrogen.}}{H^2} + \underset{\text{Parabanic acid.}}{(C^3H^2N^2O^3)}$$

It is natural that the hydrogen set free should react on parabanic acid, and give rise to leucoturic and allanturic acids and to hydantoin.

When gently heated with baryta water, hydantoin fixes $H^2O$, and is transformed into hydantoic acid ($C^3H^6N^2O^3$). This body has no analogous one in the series of alloxan; if there were one, it would be an acid derived from barbituric acid by fixing $H^2O$, and its formula would be ($C^4H^6N^2O^4$).

When alloxantin is boiled with hydrochloric acid, a new body, allituric acid ($C^6H^6N^4O^4$), is formed. This body bears the same relation to allanturic acid and to hydantoin that hydurilic acid bears to barbituric and dialuric acids. As hydurilic acid represents a double molecule of dialuric acid less an atom of oxygen and a molecule of water, so also allituric acid represents a double molecule of allanturic acid less an atom of oxygen and a molecule of water:

$$\underset{\text{Dialuric acid.}}{2(C^4H^4N^2O^4)} - \underset{\text{Water.}}{H^2O} - \underset{\text{Oxygen.}}{O} = \underset{\text{Hydurilic acid.}}{(C^8H^6N^4O^6)}$$

$$\underset{\text{Allanturic acid.}}{2(C^3H^4N^2O^3)} - \underset{\text{Water.}}{H^2O} - \underset{\text{Oxygen.}}{O} = \underset{\text{Allituric acid.}}{(C^6H^6N^4O^4)}$$

And as hydurilic acid may be regarded as resulting from the combination of a molecule of dialuric acid with one of barbituric acid united with the elimination of $H^2O$, so also allituric acid may be considered as resulting from the combination of a molecule of allanturic acid with one of hydantoin with the elimination of $H^2O$ :

$$\underset{\text{Dialuric acid.}}{(C^4H^4N^2O^4)} + \underset{\text{Barbituric acid.}}{(C^4H^4N^2O^3)} = \underset{\text{Water.}}{H^2O} + \underset{\text{Hydurilic acid.}}{(C^8H^6N^4O^6)}$$

$$\underset{\text{Allanturic acid.}}{(C^3H^4N^2O^3)} + \underset{\text{Hydantoin.}}{(C^3H^4N^2O^2)} = \underset{\text{Water.}}{H^2O} + \underset{\text{Alliturie acid.}}{(C^6H^6N^4O^4)}$$

The nitrous and nitric derivatives of hydantoin corresponding to violuric and dilituric acids and to violantin have not as yet been prepared, neither has monobrominated nor bibrominated hydantoin corresponding to monobromo- and bibromo-barbituric acids as yet been obtained.

To sum up, there exist seven derivatives of parabanic acid which are to this acid what its derivatives are to alloxan :

Parabanic acid $C^3H^2N^2O^3$.

Oxaluric acid $C^3H^4N^2O^4$ = parabanic acid, plus a molecule of water.

Oxalic acid $C^2H^2O^4$.

Oxalantin or leucoturic acid $C^6H^6N^4O^6$ = two molecules of parabanic acid, plus $H^2$.

Allanturic acid $C^3H^4N^2O^3$ = a molecule of parabanic acid, plus $H$ .

Alliturie acid $C^6H^6N^4O^4$ = two molecules of allanturic acid, less $H^2O$, and O.

Hydantoin $C^3H^4N^2O^2$ = allanturic acid, less an atom of oxygen.

Hydantoic acid $C^3H^6N^2O^3$ = a molecule of hydantoin, plus $H^2O$.

In order to show the parallelism existing between these different series, we will write them in order :

$$\underset{\text{Alloxan.}}{C^4H^2N^2O^4} - CO = \underset{\text{Parabanic acid.}}{C^3H^2N^2O^3}$$

$$\underset{\text{Alloxanic acid.}}{C^4H^4N^2O^5} - CO = \underset{\text{Oxaluric acid.}}{C^3H^4N^2O^4}$$

$$\underset{\text{Mesoxalic acid.}}{C^3H^2O^5} - CO = \underset{\text{Oxalic acid.}}{C^2H^2O^4}$$

$$\underset{\text{Alloxantin.}}{C^8H^6N^4O^8} - 2CO = \underset{\text{Leucoturic acid (oxalantin).}}{C^6H^6N^4O^6}$$

$$\underset{\text{Dialuric acid.}}{C^4H^4N^2O^4} - CO = \underset{\text{Allanturic acid.}}{C^3H^4N^2O^3}$$

$$\underset{\text{Hydurilic acid.}}{C^8H^6N^4O^6} - 2CO = \underset{\text{Alliturie acid.}}{C^6H^6N^4O^4}$$

$$\underset{\text{Barbituric acid.}}{C^4H^4N^2O^3} - CO = \underset{\text{Hydantoin.}}{C^3H^4N^2O^2}$$

$$\underset{\text{Bromo-barbituric acid.}}{C^4H^3BrN^2O^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad .$$

$C^4H^2Br^2N^2O^3$ . . . . . . . . . . .
Bibromo-barbituric acid.

$C^4H^3(NO)N^2O^3$ . . . . . . . . . . .
Violuric acid.

$C^4H^3(NO^2)N^2O^3$ . . . . . . . . . . .
Dilituric acid.

$C^8H^6(NO,NO^2)N^4O^6$ . . . . . . . . .
Violantin.

. . . . . . . . . . $C^3H^6N^2O^3$
Hydantoic acid.

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In the parabanic group there are also included:

1st. Allantoin, which is produced when uric acid is heated with water and peroxide of lead:

$$\underset{\text{Uric acid.}}{(C^5H^4N^4O^3)} + \underset{\text{Water.}}{(H^2O)} + \underset{\text{Plumbic anhydride.}}{(PbO^2)} = \underset{\text{Carbonate of lead.}}{\left(\left.\begin{matrix}CO''\\ Pb''\end{matrix}\right\} O^2\right)} + \underset{\text{Allantoin.}}{(C^4H^6N^4O^3)}$$

and which is found ready formed in the amniotic liquid of the cow. Acted upon by hydriodic acid, allantoin splits up into hydantoin and urea, and iodine is deposited:

$$\underset{\text{Allantoin.}}{(C^4H^6N^4O^3)} + \underset{\text{Hydriodic acid.}}{2\left(\left.\begin{matrix}H\\ I\end{matrix}\right\}\right)} = \underset{\text{Iodine.}}{\left.\begin{matrix}I\\ I\end{matrix}\right\}} + \underset{\text{Urea.}}{(CH^4N^2O)} + \underset{\text{Hydantoin.}}{(C^3H^4N^2O^2)}$$

2nd. Tribromacetyl-urea ($C^3H^3Br^3N^2O^2$), obtained by causing chlorine or bromine to act on bibromo-barbituric acid in presence of water:

$$\underset{\text{Bibromo-barbituric acid.}}{(C^4H^2Br^2N^2O^3)} + \underset{\text{Water.}}{(H^2O)} + \underset{\text{Bromine.}}{Br^2} = \underset{\text{Carbonic anhydride.}}{(CO^2)}$$

$$+ \underset{\text{Hydrobromic acid.}}{(HBr)} + \underset{\text{Tribromacetylic urea.}}{(C^3H^3Br^3N^2O^2)}$$

3rd. Isobiuret ($C^2H^5N^3O^2$), arising from the reaction of ammonia with tribromacetyl-urea:

$$\underset{\text{Tribromacetylic urea.}}{(C^3H^3Br^3N^2O^2)} + \underset{\text{Ammonia.}}{(NH^3)} = \underset{\text{Isobiuret.}}{(C^2H^5N^3O^2)} + \underset{\text{Bromoform.}}{(CHBr^3)}$$

4th. Bromacetyl-urea, which may be obtained by causing the bromide of brominated acetyl to act on urea:

$$\underset{\text{Bromide of brominated acetyl.}}{(C^2H^2BrO.Br)} + \underset{\text{Urea.}}{(CH^4N^2O)} = \underset{\text{Bromacetyl-urea.}}{(C^3H^5BrN^2O^2)} + \underset{\text{Hydrobromic acid.}}{HBr}$$

Hydantoin may be prepared synthetically by means of bromacetyl-urea, which must be heated with an alcoholic solution of ammonia. A molecule of hydrobromic acid is separated, and the bromacetyl-urea is transformed into glycolyl-urea or hydantoin:

$$\underset{\text{Bromacetyl-urea.}}{(C^3H^5BrN^2O^2)} + \underset{\text{Ammonia.}}{(NH^3)} = \underset{\text{Ammonic bromide.}}{(NH^4Br)} + \underset{\text{Hydantoin.}}{(C^3H^4N^2O^2)}$$

To alloxan, to alloxantin, and to dialuric and oxaluric acids, there correspond amides, which we will proceed to examine.

If hot alloxan be treated with ammonia, a body is obtained which is called mycomelic acid, and which is alloxanamide, having the formula $(C^4H^4N^4O^2)$:

$$\underset{\text{Alloxan.}}{(C^4H^2N^2O^4)} + \underset{\text{Ammonia.}}{2(NH^3)} = \underset{\text{Water.}}{2(H^2O)} + \underset{\text{Alloxanamide.}}{(C^4H^4N^4O^2)}$$

When a solution of ammonic chloride is added to a solution of alloxantin, dialuramide (uramil) $(C^4H^5N^3O^3)$, alloxan, and hydrochloric acid are produced:

$$\underset{\text{Alloxantin.}}{(C^8H^6N^4O^8)} + \underset{\text{Chloride of ammonium.}}{(NH^4Cl)} = \underset{\text{Dialuramide (uramil).}}{(C^4H^5N^3O^3)} + \underset{\text{Alloxan.}}{(C^4H^2N^2O^4)}$$

$$+ \underset{\text{Hydrochloric acid.}}{(HCl)} + \underset{\text{Water.}}{(H^2O)}$$

On causing oxide of silver or mercuric oxide to act on dialuramide, so as to oxidize this body slowly, purpurate of ammonium, called also murexid, is obtained. This body is none other than the ammoniacal salt of alloxantinamide (purpuric acid), as yet unknown in the free state:

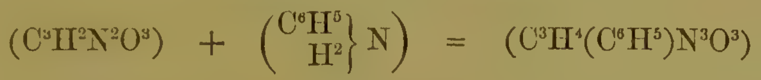
$$\underset{\text{Dialuramide.}}{2(C^4H^5N^3O^3)} + \underset{\text{Oxygen.}}{O} = \underset{\text{Purpurate of ammonium.}}{(C^8H^4(NH^4)N^5O^6)} + \underset{\text{Water.}}{\left(\begin{matrix}H\\H\end{matrix}\Big\}O\right)}$$

MM. Rosing and Schischkoff have obtained a body which they call oxalan by treating alloxan with ammonia in presence of hydrocyanic acid: the formula of oxalan is $(C^3H^5N^3O^3)$, and is formed according to the following equation:

$$\underset{\text{Alloxan.}}{2(C^4H^2N^2O^4)} + \underset{\text{Water.}}{(H^2O)} + \underset{\text{Ammonia.}}{(NH^3)} = \underset{\text{Oxalan.}}{(C^3H^5N^3O^3)}$$

$$+ \underset{\text{Dialuric acid.}}{(C^4H^4N^2O^4)} + \underset{\text{Carbonic anhydride.}}{CO^2}$$

M. Strecker has shown that this body should be regarded as oxaluramide: on substituting ethylamine, aniline, or toluidine for ammonia in this process, he has succeeded in preparing compounds which represent oxalan, one atom of hydrogen of which is replaced by ethyl, phenyl, or benzoyl. Now the product which contains phenyl is identical with phenyl-oxaluramide (oxaluranilide) obtained by Laurent and Gerhardt by the direct action of aniline on parabanic acid:



$$\underset{\text{Parabanic acid.}}{(C^3H^2N^2O^3)} + \underset{\text{Aniline.}}{\left(\left.\begin{matrix}C^6H^5\\H^2\end{matrix}\right\}N\right)} = \underset{\text{Phenyl-oxaluramide.}}{(C^3H^4(C^6H^5)N^3O^3)}$$

Thionuric acid $(C^4H^5N^3O^4.SO^2)$ must be added to the preceding compounds. It contains the elements of alloxan, ammonia, and sulphurous anhydride, and is prepared by transmitting a current of sulphurous anhydride through a boiling solution of alloxan in ammonia:

$$\underset{\text{Alloxan.}}{(C^4H^2N^2O^4)} + \underset{\text{Ammonia.}}{(NH^3)} + \underset{\text{Sulphurous anhydride.}}{(SO^2)} = \underbrace{(C^4H^5N^3SO^6) = (C^4H^5N^3O^4,SO^2)}_{\text{Thionuric acid.}}$$

The solution of thionuric acid becomes cloudy on boiling, sulphuric acid is set free, and dialuramide is deposited:

$$\underset{\text{Thionuric acid.}}{(C^4H^5N^3O^4,SO^2)} + \underset{\text{Water.}}{(H^2O)} = \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Dialuramide.}}{(C^4H^5N^3O^3)}$$

In order to understand the manner in which all these ammoniacal derivatives are formed, it must be borne in mind that under the influence of reducing bodies alloxan fixes hydrogen, and is transformed into dialuric acid; that this latter loses hydrogen when submitted to oxidation, and re-forms alloxan, and finally, that alloxantin is a combination of alloxan and dialuric acid.

If alloxan be treated with ammonia, these two bodies unite, eliminating water, and producing alloxanamide (mycomelic acid).

If sulphurous anhydride be made to take part in the reaction, a simple combination of the bodies in question takes place; but if heat be used, the sulphurous anhydride, which is a reducing agent, passes to the state of sulphuric acid, and dialuramide is formed.

It will be conceived that dialuramide will also be formed when alloxantin is submitted to the action of an ammoniacal salt, but then alloxan would be set free.

It is also to be expected that on oxidizing dialuramide it will be converted into alloxantinamide by losing hydrogen.

Recently, M. Baeyer, to whom we owe all the compounds which have lately been discovered in the uric acid series, has observed that uramil is formed when violuric or dilituric acid is treated with nascent hydrogen. This reaction is analogous to that in which oxybenzamide is formed, by causing nascent hydrogen to act on nitrobenzoic acid. It must not be forgotten that dialuric is identical with oxybarbituric acid, and that dilituric is nitrobarbituric acid:

$$\underset{\text{Nitrobenzoic acid.}}{(C^7H^5(NO^2)O^2)} + \underset{\text{Hydrogen.}}{H^6} = \underset{\text{Water.}}{2(H^2O)} + \underset{\text{Oxybenzamide.}}{(C^7H^7NO^2)}$$

$$\underset{\text{Dilituric acid.}}{(C^4H^3(NO^2)N^2O^3)} + \underset{\text{Hydrogen.}}{H^6} = \underset{\text{Water.}}{2(H^2O)} + \underset{\text{Dialuramide.}}{(C^4H^5N^3O^3)}$$

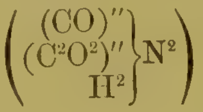
M. Bæyer has also observed that dialuramide absorbs the vapours of cyanic acid, and produces a new acid, which differs from uric acid by the addition of a molecule of water: he calls this pseudo-uric acid:

$$\underset{\text{Uramil.}}{(C^4H^5N^3O^3)} + \underset{\text{Cyanic acid.}}{(CNHO)} = \underset{\text{Pseudo-uric acid.}}{(C^5H^6N^4O^4)}$$

**Constitution of the Uric Acid Compounds.**—According to M. Bæyer, the two groups of compounds just reviewed have a similar constitution, and only differ in the nature of the radicles they contain. They are all derived either from urea, the hydrogen of which is replaced by compound radicles, or according to a mixed type of a molecule of urea and water, or of a molecule of ammonia and urea, the ammonia or water being united to the urea by means of a polyatomic radicle. The bodies derived from simple urea he calls *ureides*, those derived from the mixed urea and water type he designates as *uramic acids*, and those from the mixed urea and ammonia type he calls *uramides*. The compounds derived from a double molecule of urea, and which consequently contain four atoms of nitrogen, he calls *biureides*.

The parabanic group is the more simple of the two. The radicles which act in it are acetyl ($C^2H^3O$) or its derivatives by substitution, glycolyl ($C^2H^2O''$), oxalyl ($C^2O^{2''}$), and glyoxylyl ($C^2OH'''$).

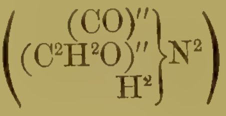
Parabanic acid is derived from oxalyl-urea:



$$\left(\left.\begin{matrix}(CO)''\\(C^2O^2)''\\H^2\end{matrix}\right\}N^2\right) = (C^3H^2N^2O^3)$$

Parabanic acid.

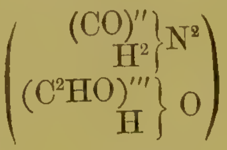
Hydantoin is from glycolyl-urea:



$$\left(\left.\begin{matrix}(CO)''\\(C^2H^2O)''\\H^2\end{matrix}\right\}N^2\right) = (C^3H^4N^2O^2)$$

Hydantoin.

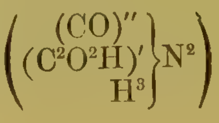
Allanturic is an uramic acid, that is to say, a body derived from the mixed urea and water type, by the substitution of the triatomic radicle of glyoxylic acid ($C^2HO'''$) for $H^3$:



$$\left(\begin{matrix}\left.\begin{matrix}(CO)''\\H^2\end{matrix}\right\}N^2\\\left.\begin{matrix}(C^2HO)'''\\H\end{matrix}\right\}O\end{matrix}\right) = (C^3H^4N^2O^3)$$

Allanturic acid.

Or, what is better, a simple ureide:



$$\left(\left.\begin{matrix}(CO)''\\(C^2O^2H)'\\H^3\end{matrix}\right\}N^2\right)$$

if the formula $\left(\left.\begin{array}{r}(C^2O^2H)'\\H\end{array}\right\}O\right)$ be adopted for glyoxylic acid, in accordance with Dr. Debus' late experiments.

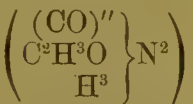
Allantoin is a compound of allanturic acid and urea; leucoturic acid is a compound of allanturic and parabanic acids; allituric acid is a compound of allanturic acid and hydantoin. These three bodies result from the addition of all the elements of their components with the elimination of $H^2O$. They contain four atoms of nitrogen, and may be regarded as biureides.

Oxaluric is an uramic acid, containing the radicle oxalyl $(C^2O^2)''$, and hydantoic acid is an uramic acid containing the radicle glycolyl $(C^2H^2O)''$.

Oxaluramide and biuret are uramides.

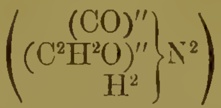
The rational formulæ of all the compounds of the parabanic group are included in the following table:

### UREIDES.



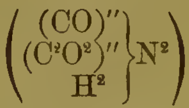
$$\left(\left.\begin{array}{r}(CO)''\\C^2H^3O\\H^3\end{array}\right\}N^2\right)$$

Acetyl-urea (and its brominated derivatives).



$$\left(\left.\begin{array}{r}(CO)''\\(C^2H^2O)''\\H^2\end{array}\right\}N^2\right)$$

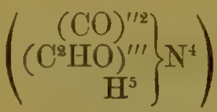
Hydantoin.



$$\left(\left.\begin{array}{r}(CO)''\\(C^2O^2)''\\H^2\end{array}\right\}N^2\right)$$

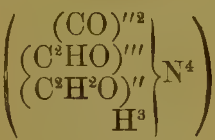
Parabanic acid.

### BIUREIDES.



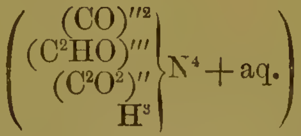
$$\left(\left.\begin{array}{r}(CO)''^2\\(C^2HO)'''\\H^5\end{array}\right\}N^4\right)$$

Allantoin (glyoxylic biureide).



$$\left(\left.\begin{array}{r}(CO)''^2\\(C^2HO)'''\\(C^2H^2O)''\\H^3\end{array}\right\}N^4\right)$$

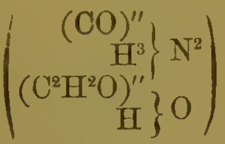
Alliturie acid (glyoxyl-glycolic biureide).



$$\left(\left.\begin{array}{r}(CO)''^2\\(C^2HO)'''\\(C^2O^2)''\\H^3\end{array}\right\}N^4+\text{aq.}\right)$$

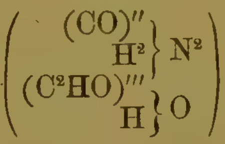
Leucoturic acid (glyoxyl-oxalic biureide).

### URAMIC ACIDS.



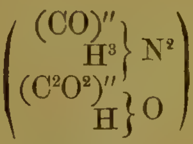
$$\left(\begin{array}{r}\left.\begin{array}{r}(CO)''\\H^3\end{array}\right\}N^2\\(C^2H^2O)''\\\left.H\right\}O\end{array}\right)$$

Hydantoic acid.



$$\left(\begin{array}{r}\left.\begin{array}{r}(CO)''\\H^2\end{array}\right\}N^2\\(C^2HO)'''\\\left.H\right\}O\end{array}\right)$$

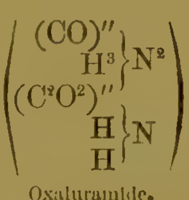
Allanturic acid.



$$\left(\begin{array}{r}\left.\begin{array}{r}(CO)''\\H^3\end{array}\right\}N^2\\(C^2O^2)''\\\left.H\right\}O\end{array}\right)$$

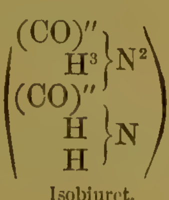
Oxaluric acid.

### URAMIDES.



$$\left(\begin{array}{r}\left.\begin{array}{r}(CO)''\\H^3\end{array}\right\}N^2\\(C^2O^2)''\\\left.\begin{array}{r}H\\H\end{array}\right\}N\end{array}\right)$$

Oxaluramide.



$$\left(\begin{array}{r}\left.\begin{array}{r}(CO)''\\H^3\end{array}\right\}N^2\\(CO)''\\\left.\begin{array}{r}H\\H\end{array}\right\}N\end{array}\right)$$

Isobiuret.

The constitution of bodies of the alloxan group may be explained by similar formulæ. But instead of the radicles of acetic, glycolic, oxalic, and glyoxylic acids, these compounds contain the radicles of malonic acid $(C^3H^2O^2)''$, tartronic or oxymalonic acid $(C^3H^2O^3)'' = (C^3H[OH]O^2)''$, and mesoxalic acid $(C^3O^3)''$, derived from malonyl by the substitution of O for $H^2$:

| $(C^3H^2O^2)''$ | $(C^3O^3)''$ |
|---|---|
| Malonyl. | Mesoxalyl. |

There is the same relation between acetyl and glycolyl as between malonyl and triatomic tartronyl $(C^3HO^2)'''$:

| $(C^2H^3O)'$ | $(C^2H^2O)''$ |
|---|---|
| Acetyl. | Glycolyl. |
| $(C^3H^2O^2)''$ | $(C^3HO^2)'''$ |
| Malonyl. | Tartronyl. |

There is also the same relation between malonyl and mesoxalyl as between glycolyl and oxalyl:

| $(C^2H^2O)''$ | $(C^2O^2)''$ |
|---|---|
| Glycolyl. | Oxalyl. |
| $(C^3H^2O^2)''$ | $(C^3O^3)''$ |
| Malonyl. | Mesoxalyl. |

The result is, that the compounds of the alloxan group present the same relations to each other as those of the parabanic acid group.

We will give a table of the rational formulæ of the principal compounds of the alloxan group, as we have done with those of the parabanic group:

UREIDES.

$$\left(\left.\begin{matrix}(CO)'' \\ (C^3H^2O^2)'' \\ H^2\end{matrix}\right\} N^2\right)$$

Barbituric acid (malonyl-urea).

$$\left(\left.\begin{matrix}(CO)'' \\ (C^3H[OH]O^2)'' \\ H^2\end{matrix}\right\} N^2\right)$$

Dialuric acid (oxymalonyl-urea).

$$\left(\left.\begin{matrix}(CO)'' \\ (C^3O^3)'' \\ H^2\end{matrix}\right\} N^2\right)$$

Alloxan (mesoxalyl-urea).

BIUREIDES.

$$\left.\begin{matrix}(CO)''^2 \\ (C^3H^2O^2)'' \\ (C^3HO^2)''' \\ H^3\end{matrix}\right\} N^4$$

Hydurilic acid (malonyl-tartronylic biureide).

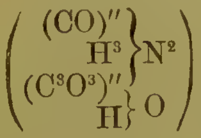
$$\left(\left.\begin{matrix}(CO)''^2 \\ (C^3HO^2)''' \\ H^5\end{matrix}\right\} N^4\right)$$

Pseudo-uric acid (tartronylic biureide).

$$\left(\left.\begin{matrix}(CO)''^2 \\ (C^3HO^2)''' \\ (C^3O^3)'' \\ H^3\end{matrix}\right\} N^4 + aq.\right)$$

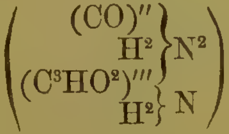
Alloxantin (tartronyl-mesoxalic biureide).

### URAMIC ACIDS.



$$\left(\begin{array}{l}\left.\begin{array}{r}(CO)''\\ H^3\\ (C^3O^3)''\end{array}\right\}N^2\\ \left.\begin{array}{r}H\end{array}\right\}O\end{array}\right)$$

Alloxanic acid.



$$\left(\begin{array}{l}\left.\begin{array}{r}(CO)''\\ H^2\\ (C^3HO^2)'''\end{array}\right\}N^2\\ \left.\begin{array}{r}H^2\end{array}\right\}N\end{array}\right)$$

Uramil.

In order to complete the study of the uric group, we must show how uric acid, the body used to prepare all these compounds, is procured.

Uric acid is generally extracted from the excrements of the boa. To effect this, these excrements are powdered, dissolved in dilute potash and boiled until ammonia is no longer disengaged. The liquid is then filtered, and a current of carbonic anhydride is passed through it, causing the formation of a white precipitate of acid urate of potassium which is almost insoluble. This precipitate is collected on a filter and washed until the washings precipitate the liquid first filtered. The acid urate thus obtained is redissolved in potash, and the solution is added to an excess of boiling hydrochloric acid. Perfectly white uric acid is precipitated, and must be collected on a filter and well washed.

Uric acid is bibasic; it is almost insoluble in water: concentrated sulphuric acid dissolves it, but water precipitates it from this solution.

When uric acid is treated by nitric acid, evaporated over a water bath, and ammonia added to the residue, there is formed murexid or diammonic purpurate (the ammoniacal salt of alloxantinamide), which presents a beautiful purple colour. This reaction is characteristic of uric acid.

DETERMINATION OF THE PROPORTION OF URIC ACID IN URINE.—A few drops of hydrochloric acid are added to a known weight of urine if it do not contain albumen; if albumen be present, acetic or phosphoric acid must be used. After 24 hours the precipitate is collected on a filter previously weighed; it is gently washed, dried and weighed. According to M. Heintz, the slight solubility of uric acid causes a loss of 0·09 per thousand of the urine used. This loss is not increased by the presence of albumen or other principles of the blood, and in all cases it is compensated by the accompanying precipitation of a certain quantity of colouring matter. However, the presence of the principles of bile may increase this loss to 0·25 per 1000.

## GUANINE, XANTHINE HYPOXANTHINE, Etc.

With uric acid must be classed three bodies which resemble it either in their composition or in their reactions. These are xanthine ($C^5H^4N^4O^2$), hypoxanthine ($C^5H^4N^4O$), and guanine ($C^5H^5N^5O$).

These three bodies exist in the organism, and may be extracted by the following processes, discovered by M. Schœrer.

To prepare xanthine or hypoxanthine, forty kilogrammes of horse-flesh free from fat is chopped up and macerated for 24 hours in cold water. This is then expressed, and the flesh boiled for a short time with a fresh quantity of water and again expressed. The cold infusion should be coagulated by heat and mixed with the decoction. Baryta water is then added until precipitation ceases; the whole is boiled, filtered, and evaporated at a gentle heat. When the liquid reaches a suitable degree of concentration, it is left in a cool place for several days; the crystals of creatine which deposit are separated, and the mother-liquor is further concentrated. By remaining at rest several days more, crystals of creatine are deposited along with a white powder which is composed of xanthine and hypoxanthine, and which may easily be separated by levigation from the crystals of creatine, which are much heavier.

This white powder must be dissolved in water, the solution added to the mother-liquors from the creatine, and acetate of copper added to the whole liquid, which must then be reduced by boiling to a small volume. An abundant precipitate is formed, which is collected on a filter and washed with boiling water until the water is no longer coloured. Then this precipitate is dissolved in dilute hydrochloric acid, a current of sulphuretted hydrogen is transmitted through the solution to precipitate the copper; the liquid is then boiled, and filtered while boiling.

When concentrated, the liquid deposits crystalline crusts which are separated as they form. When the concentration is sufficiently advanced, the liquid on cooling becomes a thick mass full of needles, which, when purified by several crystallizations from hydrochloric acid and decolorized by animal charcoal, constitute hydrochlorate of hypoxanthine; when decomposed by ammonia, they give hypoxanthine ($C^5H^4N^4O$).

The crystalline crusts are purified in the same manner: they constitute hydrochlorate of xanthine, which with ammonia gives xanthine ($C^5H^4N^4O^2$).

In order to obtain guanine, the pancreas is submitted to the treatment just described; crystalline crusts of hydrochlorate of xanthine are deposited, and at the same time prismatic crystals, which consist not of hydrochlorate of hypoxanthine, but of hydrochlorate of guanine, from which pure guanine ($C^5H^5N^5O$) is separated by ammonia.

Guanine may also be extracted from guano. To effect this, guano is boiled with lime and water until the liquid assumes a slightly green colour; it is filtered, and a quantity of hydrochloric acid sufficient to render it neutral is added: a precipitate is formed which is composed of guanine and uric acid in about equal parts. This is treated with boiling hydrochloric acid, which takes up the guanine, and this is then separated from its hydrochlorate by means of ammonia.

**Hypoxanthine** is very slightly soluble in cold water, more soluble in boiling water, and is in the form of a beautiful white powder.

The solution of hypoxanthine gives a green flocculent precipitate when heated with acetate of copper. It is also precipitated by nitrate of silver. This precipitate is soluble in boiling nitric acid, from which, on cooling, it is deposited in microscopic crystals.

Hypoxanthine dissolves in the mineral acids and in ammonia. When treated with nitric acid, evaporated, and ammonia added to the residue, this remains white or slightly yellow: the product of the action of nitric acid on hypoxanthine furnishes xanthine under the influence of reducing agents. Nitric acid therefore acts on hypoxanthine both as an oxidizing agent and as an agent of substitution.

**Xanthine** also is nearly insoluble in water, but it readily dissolves in the caustic alkalies and ammonia. The ammoniacal solution is precipitated when hot by the acetate of copper.

Carbonic anhydride separates xanthine from its solution in potash: evaporated with nitric acid, it leaves a nitrogenized product of a yellow colour, which becomes violet on contact with soda. This product reforms xanthine when submitted to reducing actions. Xanthine is rather a weak base.

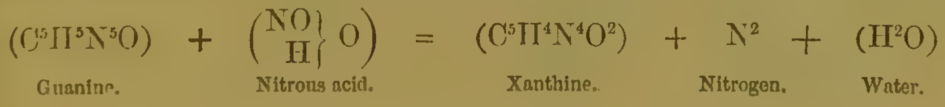
**Guanine** is a yellow powder, insoluble in water, alcohol, and ether. It combines with strong acids to form salts, which, however, are very slightly stable. Water decomposes them, and when the acid is volatile, heat destroys the combination. The alkalies dissolve guanine still better than acids.

Guanine bears the same relation to xanthine that amidated acids do to the acids whence they are derived. The following equations show these relations:

$$\underset{\text{Xanthine.}}{(C^5H^4N^4O^2)} - (HO) + (NH^2) = \underset{\text{Guanine.}}{(C^5H^5N^5O)}$$

$$\underset{\text{Lactic acid.}}{(C^3H^6O^3)} - HO + NH^2 = \underset{\text{Lactamidic acid (alanine).}}{(C^3H^7NO^2)}$$

Acted upon by nitrous acid, guanine is transformed into xanthine; but, as in order to cause nitrous acid to act on guanine, it is necessary to dissolve it in nitric acid, instead of xanthine a nitric derivative is obtained which furnishes xanthine under the influence of reducing agents. Not taking into account the intermediate nitric product, the transformation of guanine into xanthine is explained by the following equation:



$$\underset{\text{Guanine.}}{(C^5H^5N^5O)} + \underset{\text{Nitrous acid.}}{\left(\left.\begin{matrix}NO\\H\end{matrix}\right\}O\right)} = \underset{\text{Xanthine.}}{(C^5H^4N^4O^2)} + \underset{\text{Nitrogen.}}{N^2} + \underset{\text{Water.}}{(H^2O)}$$

Xanthine is thus a common term towards which guanine and hypoxanthine converge.

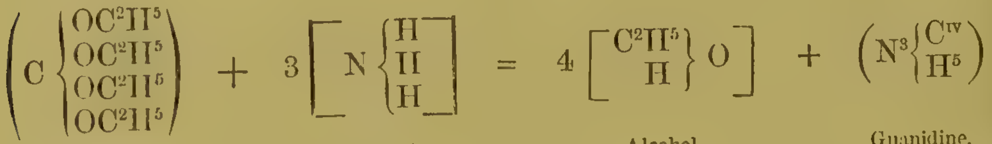
When guanine is treated with a mixture of hydrochloric acid and potassic chlorate, parabanic acid,—a new base, guanidine ($CH^5N^3$),—and a little xanthine are obtained. This reaction attaches guanine to the uric acid group, to which parabanic acid belongs.

Guanidine is a powerful base. It attracts the water and carbonic anhydride of the air, and gives rise to a carbonate:

$$[(CH^5N^3)^2,H^2O,CO^2].$$

The salts of guanidine are in general well crystallized. Guanidine may be considered as a triple molecule of ammonia in which $H^4$ would be replaced by tetratomic C, as the rational formula $\left(\left.\begin{matrix}C^{IV}\\H^5\end{matrix}\right\}N^3\right)$ indicates. M. Strecker prefers to write this body $\left(\left.\begin{matrix}CN\\H^5\end{matrix}\right\}N^2\right)$; but with this formula we do not see how two molecules of ammonia can hold together without any polyatomic radicle to unite them.

It has been seen that Hofmann has obtained guanidine by causing ammonia to act on the ortho-carbonate of ethyl:



$$\left(C\left\{\begin{matrix}OC^2H^5\\OC^2H^5\\OC^2H^5\\OC^2H^5\end{matrix}\right.\right) + 3\left[N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.\right] = 4\left[\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right] + \left(N^3\left\{\begin{matrix}C^{IV}\\H^5\end{matrix}\right.\right)$$

Ortho-carbonate of ethyl. Ammonia. Alcohol. Guanidine.

## CREATINE, CREATININE.

We have already said that a crystallized substance called creatine may be extracted from muscular tissue. The formula of this substance is $C^4H^9N^3O^2 + aq$.

Creatine is colourless, pearl-like, without taste, and without action on test-paper. It is much more soluble in hot than in cold water, less soluble in alcohol, and insoluble in ether.

In presence of strong acids creatine loses water, and is transformed into creatinine:

$$\underset{\text{Creatine.}}{(C^4H^9N^3O^2)} = \underset{\text{Water.}}{(H^2O)} + \underset{\text{Creatinine.}}{(C^4H^7N^3O)}$$

When boiled with baryta water it splits up into urea and sarkosine (methyl-glycocol), assimilating the elements of water:

$$\underset{\text{Creatine.}}{(C^4H^9N^3O^2)} + \underset{\text{Water.}}{(H^2O)} = \underset{\text{Urea.}}{(CH^4N^2O)} + \underset{\text{Sarkosine.}}{(C^3H^7NO^2)}$$

Under the influence of oxidants, creatine furnishes methyluramine ($C^2H^7N^3$), which may be considered as methylguanidine $\left(\left.\begin{matrix}C^{IV}\\CH^3\\H^4\end{matrix}\right\}N^3\right)$.

When submitted to the action of nitrous acid, creatine, according to M. Dessaignes, is converted into a substance having the composition ($C^4H^4N^2O^2$), and which appears to be methylparabanic acid ($C^3H(CH^3)N^2O^3$). This body is also produced by the action of nitrous acid on creatinine.

With chloride of zinc the hydrochlorates of creatine and creatinine form double salts, nearly insoluble and well crystallized.

As, by the action of baryta, creatine, absorbing the elements of water, is split up into methyl-glycocol and urea, and as, moreover, cyanamide, by uniting with a molecule of water, may be transformed into urea, M. Strecker thinks that creatine should be considered as a compound of cyanamide and methyl-glycocol.

Guided by these considerations, M. Strecker mixed solutions of glycocol and cyanamide along with a few drops of ammonia; he thus produced a body having the formula ($C^3H^7N^3O^2$), which differs from creatine by the substitution of H for ($CH^3$), and which he calls glyco-cyamine. It is a feeble base; its hydrochlorate loses $H^2O$ at 160°, and is converted into the hydrochlorate of a new base, glyco-cyamidine ($C^3H^5N^3O$), which is to glyco-cyamine what creatinine is to creatine.

The production of glyco-cyamine appears to justify M. Strecker's views as to the constitution of creatine.

## THEOBROMINE AND CAFFEINE.

A substance called theobromine ($C^7H^8N^4O^2$) is extracted from the cacao-nut, and another substance called caffeine, the composition of which is expressed by the formula ($C^8H^{10}N^4O^2$), is extracted from coffee.

Strecker has shown that caffeine is a methylated derivative of theobromine: on treating the latter with an ammoniacal solution of nitrate of silver, he obtained a crystalline precipitate which, when dried at 120°, had the formula ($C^7H^7AgN^4O^2$). When submitted to the action of iodide of methyl, this body gives rise to iodide of silver and caffeine:

$$\underset{\text{Argentic theobromine.}}{(C^7H^7AgN^4O^2)} + \underset{\substack{\text{Iodide of}\\\text{methyl.}}}{\left(\left.\begin{matrix}CH^3\\I\end{matrix}\right\}\right)} = \underset{\substack{\text{Iodide of}\\\text{silver.}}}{\left.\begin{matrix}Ag\\I\end{matrix}\right\}} + \underset{\text{Caffeine.}}{(C^7H^7(CH^3)N^4O^2)}$$

Caffeine, when acted upon by oxidizing agents, gives two bodies of the uric acid group, tetra-methyl-alloxantine ($C^8(CH^3)^4H^2N^4O^8$) (amalic acid), and dimethyl-parabanic acid ($C^3(CH^3)^2N^2O^3$) (cholestrophan).

These products attach theobromine and caffeine to the uric acid group; moreover, theobromine appears to be a homologue of xanthine:

$C^5H^4N^4O^2$ . . . . . . . . . xanthine.
$C^7H^8N^4O^2$ . . . . . . . . . theobromine.

At any rate, it is certain that theobromine is not dimethylated xanthine. On treating diargentic xanthine ($C^5H^2Ag^2N^4O^2$) with iodide of methyl, M. Strecker has in reality obtained dimethyl-xanthine, which is isomeric and not identical with theobromine.

M. Strecker's researches thus prove that caffeine and theobromine approach the uric acid group; that xanthine, guanine, and hypoxanthine are joined to this group and intimately related to each other; that creatine and creatinine are also attached to the uric acid group; and that the synthesis of creatine may be hoped for.

We have yet to give these bodies rational formulæ which would show their relations and their transformations: this has been attempted for several of them, but the formulæ proposed do not appear to me to be sufficiently general; and, in short, this is a work which still remains to be accomplished.

## ALBUMINOID SUBSTANCES.

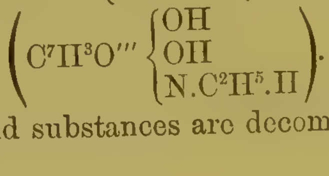
These substances are found in abundance in the liquids and tissues of animals, as well as in certain organs of vegetables; they are all uncrystallizable, contain sulphur among the number of their elements, and are decomposed when it is attempted to distil them, disengaging sulphide of ammonium among other products.

Fuming hydrochloric acid dissolves albuminoid substances: the solution assumes a blue colour in the air; protected from the air, it remains yellow.

Under the influence of the acid liquid which is obtained by dissolving mercury in its own weight of nitric acid, albuminoid substances assume an intense red colour: this reaction detects one part of albumen in 100,000 parts of water.

Potash dissolves all albuminoid substances. When this solution is boiled, a liquid is obtained from which the acids disengage hydrosulphuric acid and precipitate a substance known as protein.

All albuminoid substances furnish the same products when oxidized. These products belong either to the aromatic series or to that of the fatty acids. Thus, benzoic aldehyd, benzoic acid, acetic, propylic, and valeric aldehyds, acetic, propionic, butyric, and valeric acids are obtained, as is also a product called tyrosine ($C^9H^{11}NO^3$), which appears to be ethyl-amido-paroxybenzoic acid



$$\left(C^7H^3O'''\left\{\begin{matrix}OH\\OH\\N.C^2H^5.H\end{matrix}\right.\right).$$

When exposed to the air albuminoid substances are decomposed, and transformed into new bodies which are not well defined. This great instability of the albuminoid principles is a characteristic which clearly distinguishes them from other organic principles. Certain substances in this group, simply by their presence, cause the hydration of other bodies by means of decomposition. Diastase, which is extracted from germinated barley, possesses this property in a high degree. For a long time these substances have been called ferments; but M. Pasteur having demonstrated that fermentations are owing to the development of organisms to which the name of ferments should properly be applied, this name is not suitable for the substances just spoken of.

There exist three well-characterized albuminoid principles—albumen, fibrin, and casein: the others are little known and are possibly only mixtures.

Albumen is found in the white of egg, in the serous portion of the blood, and in other fluids of the economy. M. Wurtz has shown that the albumen of the blood and that of the egg are not identical. These two liquids are precipitated by acetate of lead; but while a current of sulphuretted hydrogen re-forms soluble albumen from the plumbic precipitate obtained from the white of egg, such is not the case with that procured from the serum of the blood.

Albumen in solution is coagulated by heat, and it then becomes insoluble. A similar coagulation is produced by acids, except by acetic and phosphoric acids; and not only do these acids not coagulate albumen, but they redissolve it when coagulated.

*Fibrin* exists in the blood of animals, whence it is deposited spontaneously in a coagulated state on removing the blood from the body: it is obtained by whipping the blood, when it is deposited in small white filaments. In a chemical point of view, fibrin presents all the characters of insoluble albumen; it only differs from it by its fibrous form and by its property of decomposing oxygenized water. Fibrin enters into the composition of the seeds of cereals, etc. Mixed with another substance, gluten, it constitutes the glutinous or azotized portion of these seeds.

*Casein* is the principal azotized portion of the milk of animals: it is also found in the seeds of leguminous plants, when it is called *legumin.* It is soluble in water and not coagulated by heat; but all the acids coagulate it, even including acetic acid, which is without action on albumen, but an excess of this acid redissolves it.

The different substances in question appear identical in their elementary composition, the slight differences given by analysis may be owing to impurities, for these uncrystallizable substances cannot be completely purified. When burned, they always leave a certain quantity of ash which contains phosphate of calcium; the ashes left by albumen and casein contain, in addition, alkaline carbonates, while those left by fibrin do not.

Coagulated albumen and casein, as well as fibrin, dissolve in alkaline solutions: if the excess of alkali be removed by dialysis, a solution is obtained which possesses almost all the characters of albumen from the white of egg: on adding to this solution, as to natural soluble albumen, a large quantity of alkali, the properties of casein are communicated to it.

Starting from this point, we may reasonably suppose that in reality there only exists a single albuminoid substance, acting in the same manner as weak acids, and capable, like certain well-known bodies, of existing both in a soluble and in a coagulated state. If the name of albumen be reserved for this principle, fibrin should be considered as insoluble albumen more or less mixed with earthy phosphate, albumen as an acid albuminate of sodium, and casein as the neutral albuminate of sodium.

Many chemists, M. Wurtz among others, call in question the identity of composition of the albuminoid substances: they consider it impossible to prove the identity of a body whose molecule is so complicated, especially as these compounds cannot be obtained in a pure state for analysis. This reasoning is sound; but as, on the other hand, it cannot be shown by analysis that these substances are not identical, and as, moreover, they give the same products of decomposition, our hypothesis remains justifiable, and we shall adopt it along with Liebig, Gerhardt, and others.

## GELATINOUS SUBSTANCES.

The skin, the organic part of bones, the tendons, serous membranes, cellular tissue, the hoof of the stag, etc., are transformed by prolonged boiling into a substance which, on cooling, becomes a jelly, and is called gelatine.

Under the same conditions, the cartilages give another substance called chondrin, which resembles gelatine, and these two are the substances which we designate as gelatinous.

**Gelatine.**—We have just said that gelatine results from the action of water on the organic matter of bones (ossein), etc. It presents the same composition as ossein, and is known in commerce as glue.

The glue of commerce, however, is not pure gelatine. In order to purify it, it is allowed to become a jelly in cold water, and is separated mechanically, then washed in hot water until this is no longer coloured, when the gelatine is dissolved in water at a gentle heat: the solution is filtered to separate insoluble matters, and the gelatine is precipitated from the filtered liquid by means of alcohol.

Gelatine swells up in cold water without dissolving; it is soluble in hot water and becomes a jelly on cooling. It is modified, and loses this latter property, when submitted to prolonged boiling.

Moist gelatine left in air soon putrefies and develops a large quantity of ammonia.

When gelatine is boiled for some time with potash, leucine, glycocol, and other undetermined bodies are produced. Glycocol is also produced by the action of cold concentrated sulphuric acid on gelatine, and it is owing to this that glycocol is improperly called sugar of gelatine.

By dry distillation, gelatine gives different alkaloids (piccoline, lutidine, pyrridine, methylamine, etc.), undetermined neutral oils, along with ammonic carbonate and hydrocyanate.

Nitric acid converts gelatine into several products, among which saccharic acid appears to be one.

Tannin gives an insoluble precipitate with gelatine; analogous compounds are produced when tannin is made to act on the different substances which furnish gelatine, and these compounds do not putrefy. The tanning of leather is founded on this property.

In general, metallic salts do not precipitate gelatine. Under the influence of a mixture of peroxide of manganese and sulphuric acid, that is to say of oxidizing agents, gelatine furnishes the same products as the albuminoid substances.

Gerhardt has obtained glucose and sulphate of ammonium by boiling gelatine for several days with dilute sulphuric acid. This experiment tends to justify an hypothesis of Mr. Hunt, according to which gelatine would be an ammoniacal derivative of glucose. (Mr. Hunt says cellulose, but we think it necessary to say glucose, because cellulose itself should be considered as a derivative of glucose. However, it is probable that if this hypothesis be correct, gelatine is derived not from ordinary glucose, but from a polyglucosic alcohol):

$$\underset{\text{Polyglucosic alcohol.}}{(nC^6H^{12}O^6-[n-1]H^2O)} + \underset{\text{Ammonia.}}{2(nNH^3)} = \underset{\text{Gelatine.}}{(nC^6H^{10}N^2O^2)}$$

$$+ \underset{\text{Water.}}{3n+1(H^2O)}$$

In this formula a certain quantity of oxygen should be replaced by an equivalent quantity of sulphur, as gelatine is a sulphuretted body.

If it be considered that the origin we have attempted to establish for gelatine is probable, and that this body on decomposing under the influence of oxidizing agents, gives products which are identical with those furnished by the albuminoid substances, it cannot be doubted that these latter substances are related to gelatine, and consequently we must consider it probable that the albuminoid principles are also ammoniacal derivatives of polyglucosic alcohols.

Gelatine is not generally precipitated by metallic salts; alum, however, precipitates it in presence of alkalies.

**Chondrin.**—We have already seen that this substance is extracted from the cartilages; the cornea also furnishes it.

Like gelatine, chondrin swells up in cold water, and dissolves in boiling water, and also gelatinizes on cooling.

It differs from gelatine in that it is precipitated by most metallic salts.

Analysis shows that the composition of chondrin greatly resembl that of gelatine: there is, however, a difference in the quantity of nitrogen; gelatine containing 19·71, and chondrin only 14·4 per cent. of this element. The action of alkalies on chondrin furnishes very little leucine, and that of sulphuric acid gives leucine without glycocoll.

By the side of gelatine and chondrin, certain substances which appear to differ from them by several properties are placed. Such are the substance obtained by treating elastic tissue by water, and limacine, obtained by M. Braconot by boiling slugs in pure water. These substances are little known.

## ACTION OF REAGENTS ON ORGANIC COMPOUNDS.

The principal reagents used in organic chemistry are: oxygen or oxidizing agents; chlorine, bromine, and iodine; hydrochloric, hydrobromic, hydriodic, sulphuric, and nitric acids; with the chloride, bromide, and iodide of phosphorus; reducing agents, at the head of which nascent hydrogen must be placed; the alkaline bisulphites (acid sulphites), ammonia, and nitrous acid; and dehydrating agents, as the sulphide of phosphorus, the caustic alkalies, etc.

**Oxidizing Agents.**—All bodies which can give rise to a disengagement of oxygen act as oxidizing agents. Nascent oxygen often acts where free oxygen is inert.

Oxygen may act on organic substances in four different methods.

1st. It may remove hydrogen from these substances:

$$\underset{\text{Alcohol.}}{(C^2H^6O)} + \underset{\text{Oxygen.}}{O} = \underset{\text{Water.}}{(H^2O)} + \underset{\text{Aldehyd.}}{(C^2H^4O)}$$

2nd. It may be substituted for hydrogen:

$$\underset{\text{Alcohol.}}{(C^2H^6O)} + \underset{\text{Oxygen.}}{\left.\begin{matrix}O\\O\end{matrix}\right\}} = \underset{\text{Water.}}{(H^2O)} + \underset{\text{Acetic acid.}}{(C^2H^4O^2)}$$

3rd. It may be added to the substance:

$$\underset{\text{Aldehyd.}}{(C^2H^4O)} + \underset{\text{Oxygen.}}{O} = \underset{\text{Acetic acid.}}{(C^2H^4O^2)}$$

4th. It may simplify the organic molecule, removing from it either carbon, or both carbon and hydrogen: in this case it may or may not be added to the molecule thus simplified, or the carbon eliminated may or may not take with it part of the oxygen of the substance. Thus when alloxan is treated with an oxidizing agent, an atom of carbon and an atom of oxygen are removed, and parabanic acid is left:

$$\underset{\text{Alloxan.}}{(C^4H^2N^2O^4)} + \underset{\text{Oxygen.}}{O} = \underset{\text{Carbonic anhydride.}}{(CO^2)} + \underset{\text{Parabanic acid.}}{(C^3H^2N^2O^3)}$$

When oxidizing agents act on oleic acid, two series of acids are obtained; the first homologous with formic acid, the other with oxalic acid: in this case oleic acid loses hydrogen and carbon.

Among the products formed, some result from the fixation of oxygen on the simplified molecules; such are the homologues of oxalic acid: others are the direct result of the simplification of the molecule of oleic acid, without there being any fixation of oxygen.

**Chlorine and Bromine.**—These bodies act in a similar manner on organic substances, but the action of chlorine is more powerful than that of bromine.

1st. They remove hydrogen without replacing it:

$$\underset{\text{Alcohol.}}{(C^2H^6O)} + \underset{\text{Chlorine.}}{\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}} = \underset{\text{Hydrochloric acid.}}{2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Aldehyd.}}{(C^2H^4O)}$$

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2nd. They are substituted for hydrogen:

$$\underset{\text{Toluene.}}{(C^7H^8)} + \underset{\text{Chlorine.}}{\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}} = \underset{\text{Hydrochloric acid.}}{\left.\begin{matrix}H\\Cl\end{matrix}\right\}} + \underset{\text{Monochlorinated toluene.}}{(C^7H^7Cl)}$$

3rd. They are simply added to unsaturated molecules:

$$\underset{\text{Fumaric acid.}}{(C^4H^4O^4)} + \underset{\text{Bromine.}}{\left.\begin{matrix}Br\\Br\end{matrix}\right\}} = \underset{\text{Bibromo-succinic acid.}}{(C^4H^4Br^2O^4)}$$

4th. In presence of water they seize the hydrogen of this liquid and liberate oxygen, so as to act as oxidizing agents. They may even act in a similar manner without water intervening: one portion of the organic substance is decomposed, and yields its oxygen to the other portion, in which case carbon is deposited. MM. Friedel and Machuca have observed a fact of this description: on heating bromine with butyric acid, they obtained succinic acid, the result of an oxidizing action:

$$\underset{\text{Butyric acid.}}{(C^4H^8O^2)} + \underset{\text{Oxygen.}}{3O} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Succinic acid.}}{(C^4H^6O^4)}$$

**Iodine.**—Like bromine and chlorine, iodine can act as an oxidizing agent, and can also be added directly to organic molecules, but it never gives rise to phenomena of substitution, unless the hydriodic acid be saturated as it is formed, as when iodine acts on an organic base. Generally the products of iodized substitution are prepared by an indirect method.

**Hydrochloric and Hydrobromic Acids.**—These acids give rise to phenomena of direct addition, and of double decomposition.

1st. They are added directly to unsaturated molecules. When these molecules possess basic properties, like compound ammonias, the combination takes place in the cold, with the disengagement of a considerable amount of heat; other bodies besides compound ammonias are able to combine with these hydracids in the cold:

$$\left(\left.\begin{matrix}C^2H^5\\H^2\end{matrix}\right\}N\right) + \left.\begin{matrix}H\\Cl\end{matrix}\right\} = \left.\begin{matrix}\left[\left.\begin{matrix}C^2H^5\\H^3\end{matrix}\right\}N\right]\\Cl\end{matrix}\right\}$$

Ethylamine. Hydrochloric acid. Chloride of ethyl-ammonium.

$$(C^2H^4) + \left.\begin{matrix}H\\Cl\end{matrix}\right\} = (C^2H^5Cl)$$

Ethylene. Hydrochloric acid. Chloride of ethyl.

2nd. They enter into double decomposition. Thus in presence of alcohols and acids whose atomicity is greater than their basicity, they exchange their chlorine or bromine for the group OH, forming water and a chlorinated or brominated organic product:

$$\left(\left.\begin{matrix}C^7H^7\\H\end{matrix}\right\}O\right) + \left.\begin{matrix}H\\Cl\end{matrix}\right\} = \left(\left.\begin{matrix}C^7H^7\\Cl\end{matrix}\right\}\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

Benzoic alcohol. Hydrochloric acid. Chloride of benzoyl. Water.

$$(C^3H^6O^3) + \left.\begin{matrix}H\\Br\end{matrix}\right\} = (C^3H^5BrO^2) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

Lactic acid. Hydrobromic acid. Bromopropionic acid. Water.

$$\left(\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}O\right) + 2\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right) = 2\left(\left.\begin{matrix}C^2H^5\\Cl\end{matrix}\right\}\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

Ether. Hydrochloric acid. Chloride of ethyl. Water.

**Hydriodic Acid.**—Hydriodic acid gives rise to the same phenomena of addition as its two congeners; it even combines more readily than they do, but it will not always enter into analogous double decompositions. In fact, when hydriodic acid acts on iodized bodies, it sets the iodine free, producing an inverse substitution:

$$(C^2H^3IO^2) + \left.\begin{matrix}H\\I\end{matrix}\right\} = (C^2H^4O^2) + \left.\begin{matrix}I\\I\end{matrix}\right\}$$

Iodacetic acid. Hydriodic acid. Acetic acid. Iodine.

It cannot therefore produce iodized compounds by double decomposition, unless they are formed at a temperature lower than that at which hydriodic acid would decompose them.

Under those conditions in which its congeners would give rise to double decompositions and hydriodic acid itself cannot, the latter acts as a reducing agent. This is the case with those polyatomic alcohols and acids whose atomicity is greater than their basicity :

$$\underset{\text{Lactic acid.}}{(C^3H^6O^3)} + \underset{\text{Hydriodic acid.}}{2\left(\left.\begin{matrix}H\\I\end{matrix}\right\}\right)} = \underset{\text{Propionic acid.}}{(C^3H^6O^2)} + \underset{\text{Water.}}{(H^2O)} + \underset{\text{Iodine.}}{I^2}$$

$$\underset{\text{Mannite.}}{(C^6H^{14}O^6)} + \underset{\text{Hydriodic acid.}}{11\left(\left.\begin{matrix}H\\I\end{matrix}\right\}\right)} = \underset{\text{Iodide of hexyl.}}{(C^6H^{13}I)} + \underset{\text{Water.}}{6\,(H^2O)} + \underset{\text{Iodine.}}{5\left(\left.\begin{matrix}I\\I\end{matrix}\right\}\right)}$$

It must be remarked that hydriodic acid acts as a reducing agent only on the acids whose basicity is less than their atomicity, and that it is without action on the acids whose basicity is equal to their atomicity; oxalic acid, for instance. The reason of this is that it acts on alcoholic hydroxyl, but not on acid hydroxyl.

The acids of the aromatic series whose atomicity is greater than their basicity, but the hydroxyl of which is phenic and not alcoholic, are not reduced by hydriodic acid, as M. Lautemann found with salicylic acid, and as I ascertained with thymotic acid.

Those aromatic acids, on the contrary, which contain alcoholic hydroxyl are reduced like the corresponding fatty acids. Thus M. Louguinine and myself have found that formo-benzoylic acid $(C^8H^8O^3)$, under the influence of hydriodic acid, is transformed into alphatoluic acid $(C^8H^8O^2)$.

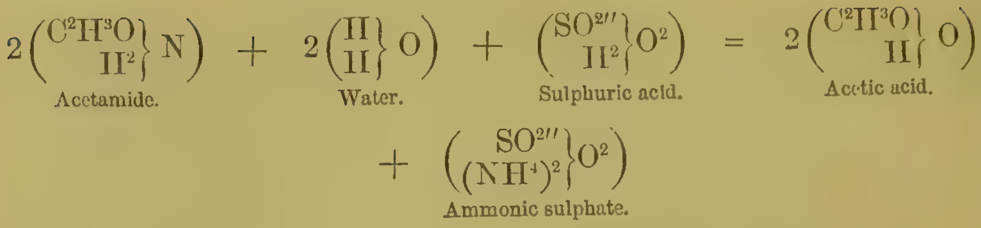
The action exercised by hydriodic acid on iodized organic compounds is the cause of iodine being unable to give rise to phenomena of substitution. Such phenomena would necessitate the production of a quantity of hydriodic acid equivalent to that of the iodine substituted, and thence the product of substitution would be decomposed as it formed.

When hydriodic acid acts on condensed polyatomic alcohols, it reduces them, and resolves them into their different generators:

$$\underset{\text{Diethylenic alcohol.}}{\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\C^2H^{4\prime\prime}\\H^2\end{matrix}\right\}O^3\right)} + \underset{\text{Hydriodic acid.}}{4\left(\left.\begin{matrix}H\\I\end{matrix}\right\}\right)} = \underset{\text{Water.}}{3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Iodide of ethylene.}}{2\left(\begin{matrix}C^2H^{4\prime\prime}\\I^2\end{matrix}\right)}$$

**Sulphuric Acid.**—Sulphuric acid may be used either diluted, concentrated, or anhydrous. Diluted, it fixes water on organic substances; under its influence, saccharose is transformed into glucose and amides into ammoniacal salts :

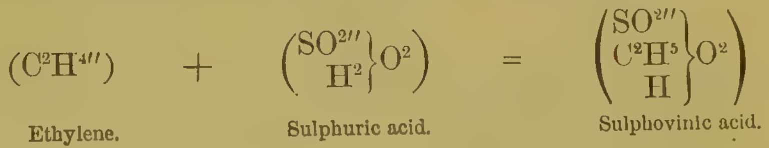
$$\underset{\text{Saccharose (cane sugar).}}{(C^{12}H^{22}O^{11})} + \underset{\text{Water.}}{(H^2O)} = \underset{\text{Glucose.}}{2(C^6H^{12}O^6)}$$



$$2\left(\left.\begin{matrix}C^2H^3O\\H^2\end{matrix}\right\}N\right) + 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}SO^{2\prime\prime}\\H^2\end{matrix}\right\}O^2\right) = 2\left(\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}SO^{2\prime\prime}\\(NH^4)^2\end{matrix}\right\}O^2\right)$$

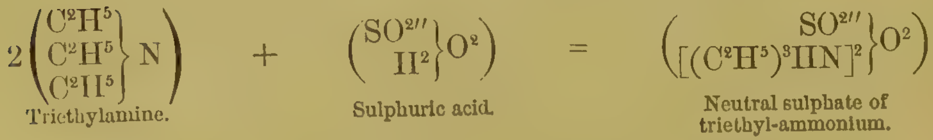
Acetamide. Water. Sulphuric acid. Acetic acid. Ammonic sulphate.

When concentrated, it can combine directly with compound ammonias, with certain hydrocarbons, with the ethers of polyatomic alcohols, etc.:



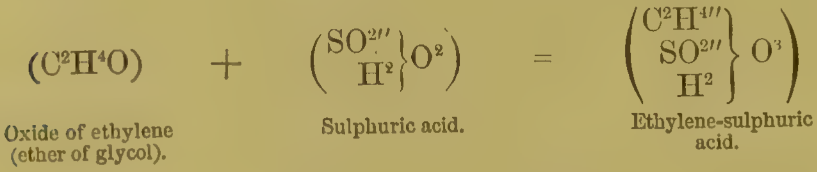
$$(C^2H^{4\prime\prime}) + \left(\left.\begin{matrix}SO^{2\prime\prime}\\H^2\end{matrix}\right\}O^2\right) = \left(\left.\begin{matrix}SO^{2\prime\prime}\\C^2H^5\\H\end{matrix}\right\}O^2\right)$$

Ethylene. Sulphuric acid. Sulphovinic acid.



$$2\left(\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right\}N\right) + \left(\left.\begin{matrix}SO^{2\prime\prime}\\H^2\end{matrix}\right\}O^2\right) = \left(\left.\begin{matrix}SO^{2\prime\prime}\\{[(C^2H^5)^3HN]^2}\end{matrix}\right\}O^2\right)$$

Triethylamine. Sulphuric acid. Neutral sulphate of triethyl-ammonium.



$$(C^2H^4O) + \left(\left.\begin{matrix}SO^{2\prime\prime}\\H^2\end{matrix}\right\}O^2\right) = \left(\left.\begin{matrix}C^2H^{4\prime\prime}\\SO^{2\prime\prime}\\H^2\end{matrix}\right\}O^3\right)$$

Oxide of ethylene (ether of glycol). Sulphuric acid. Ethylene-sulphuric acid.

When concentrated or anhydrous, it can act as a dehydrating agent, or by modifying the molecule, or by double decomposition.

1st. It acts as a dehydrating agent with the alcohols having the radicles $C^nH^{2n+1}$, transforming them into hydrocarbides $C^nH^{2n}$. But the dehydrating action of sulphuric acid is never exercised alone. Therefore the chloride of zinc or phosphoric anhydride should be preferred for the production of reactions of this order.

2nd. It modifies the molecule of certain substances, which it converts into isomers or polymers. Thus, under its influence, amylene ($C^5H^{10}$) is transformed into diamylene ($C^{10}H^{20}$); oil of turpentine is converted into an isomer which only differs from the original hydrocarbide by the absence of rotatory action on light.

3rd. It enters into double decomposition with organic substances, that is to say, it combines with these substances, eliminating water. Here two different cases may arise: either the products which are formed are capable of reproducing their generators by appropriate means, or they are not capable of so doing.

The salts which result from the reaction of sulphuric acid on organic bases, such as the hydrates of ammoniums or the hydrates of organo-metallic radicles, are instances of the first, as are also the sulphuric ethers which re-form the alcohol whence they are derived, a sulphate being at the same time formed, when they are treated with mineral bases.

As instances of the second case may be mentioned those conjugate bodies which result from the action of sulphuric acid on other organic compounds, among which certain hydrocarbons, and acids in general must be placed.

When the bodies with which sulphuric acid reacts are acid, the product is always acid. When, on the contrary, these bodies are neutral and several of their molecules act on a single molecule of sulphuric acid, the product is neutral.

Thus the following products are acid:

$$\underset{\text{Thymyl-sulphurous acid.}}{(C^{10}H^{14}SO^{3})} = \underset{\text{Cymene.}}{(C^{10}H^{14})} + \underset{\text{Sulphuric acid.}}{(SH^{2}O^{4})} - \underset{\text{Water.}}{(H^{2}O)}$$

$$\underset{\text{Phenyl-sulphurous acid.}}{(C^{6}H^{6}SO^{3})} = \underset{\text{Benzine.}}{(C^{6}H^{6})} + \underset{\text{Sulphuric acid.}}{(SH^{2}O^{4})} - \underset{\text{Water.}}{(H^{2}O)}$$

$$\underset{\text{Sulpho-benzoic acid.}}{(C^{7}H^{6}SO^{5})} = \underset{\text{Benzoic acid.}}{(C^{7}H^{6}O^{2})} + \underset{\text{Sulphuric acid.}}{(SH^{2}O^{4})} - \underset{\text{Water.}}{(H^{2}O)}$$

$$\underset{\text{Sulphanilic acid.}}{(C^{6}H^{7}NSO^{3})} = \underset{\text{Aniline.}}{(C^{6}H^{7}N)} + \underset{\text{Sulphuric acid.}}{(SH^{2}O^{4})} - \underset{\text{Water.}}{(H^{2}O)}$$

$$\underset{\text{Sulpho-succinic acid.}}{(C^{4}H^{6}SO^{7})} = \underset{\text{Succinic acid.}}{(C^{4}H^{6}O^{4})} + \underset{\text{Sulphuric acid.}}{(SH^{2}O^{4})} - \underset{\text{Water.}}{(H^{2}O)}$$

The following products are neutral:

$$\underset{\text{Sulpho-benzide.}}{(C^{12}H^{10}SO^{2})} = \underset{\text{Benzine.}}{2(C^{6}H^{6})} + \underset{\text{Sulphuric acid.}}{(SH^{2}O^{4})} - \underset{\text{Water.}}{2(H^{2}O)}$$

$$\underset{\text{Sulpho-naphthalide.}}{(C^{20}H^{14}SO^{2})} = \underset{\text{Naphthalin.}}{2(C^{10}H^{8})} + \underset{\text{Sulphuric acid.}}{(SH^{2}O^{4})} - \underset{\text{Water.}}{2(H^{2}O)}$$

It is to be remarked that all these products contain the elements of an organic substance united to those of sulphuric acid, less water. We also see that if the number of molecules reacting be represented by $n$, $n - 1$ will represent the number of molecules of water eliminated.

Gerhardt gives the following rule, whereby the basicity of a sulpho-conjugate body may be calculated, that of the bodies which form it being known.

"The basicity B of a sulpho-conjugate product is equal to the sum of the basicities of the organic matter $b$ and of sulphuric acid $b'$, less the sum $n-1$ of the molecules which enter into the reaction:"

$$B = b + b' - (n - 1).$$

For example: succinic acid has a basicity equal to 2, therefore $b = 2$; sulphuric acid is bibasic, therefore $b' = 2$; a molecule of succinic acid reacts with one of sulphuric acid to produce sulphosuccinic acid, therefore $n=2$. On replacing $b$, $b'$ and $n$ by their values in the preceding equation, it becomes:

$$B=2+2-(2-1)=3.$$

If more than one molecule of sulphuric acid or of the other body entered into the reaction, $b$ and $b'$ must be multiplied by this number: the above equation would then be written:

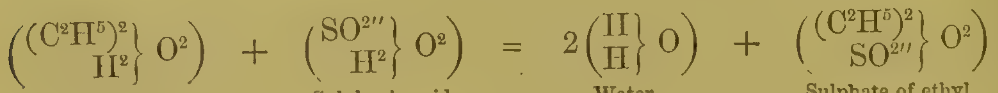
$$B=b'^{m}+b^{n}-(m+n-1),$$

$m$ and $n$ representing the number of the molecules of the bodies whose basicities are $b$ and $b'$.

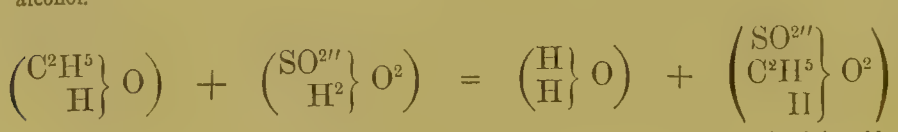
If the body reacting with sulphuric acid be neutral, we have only to make $b=o$.

It would be more correct in the preceding rule to substitute the word atomicity for basicity. But, in this latter case, this law would not be applicable to the sulpho-conjugate bodies which reproduce their generators. If it were applied to the determination of the atomicity of sulphovinic acid, that of alcohol being 1 and that of sulphuric acid being 2, 2 would be the atomicity of the product, whilst in reality it is 1.

The difference which exists between these two classes of sulpho-conjugate products is probably owing to the manner in which the substitution takes place. Sometimes the radicle of the organic substance is substituted for an equivalent quantity of typical hydrogen of the sulphuric acid; the atomicity is then equal to the sum of the atomicities of the reacting bodies, less 2 for each molecule of water eliminated; we have $B=b+b'^{m}-2n'$, $n'$ representing the number of molecules of water eliminated. In this method of substitution, the group $(SO^2)''$ remains distinct from the radicle of the original organic substance. The result is that, on fixing water, the product can be resolved into its generators:



$$\underset{\text{Two molecules of alcohol.}}{\left(\left.\begin{matrix}(C^2H^5)^2\\ H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2\prime\prime}\\ H^2\end{matrix}\right\}O^2\right)} = \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)} + \underset{\text{Sulphate of ethyl.}}{\left(\left.\begin{matrix}(C^2H^5)^2\\ SO^{2\prime\prime}\end{matrix}\right\}O^2\right)}$$



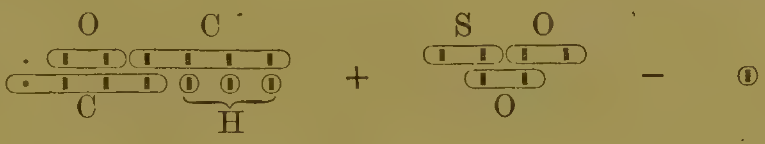
$$\underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\ H\end{matrix}\right\}O\right)} + \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2\prime\prime}\\ H^2\end{matrix}\right\}O^2\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)} + \underset{\text{Sulphovinic acid.}}{\left(\left.\begin{matrix}SO^{2\prime\prime}\\ C^2H^5\\ H\end{matrix}\right\}O^2\right)}$$

Sometimes the radicle sulphuryl $(SO^2)''$ is substituted for an equivalent quantity of hydrogen which passes to the state of water, this hydrogen eliminated being taken half from the typical hydrogen and half from that of the radicle. As the atomicity is owing to the typical hydrogen, it only diminishes by one in this case, while in the preceding it was diminished by two, and it conforms to Gerhardt's law.

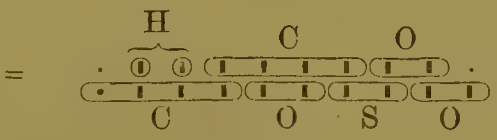
Moreover, here the group $(SO^2)''$ enters into the radicle of the sulpho-conjugate body; it is united to the molecule more closely, and this cannot reproduce its generators on becoming hydrated.

It will readily be conceived that the atomicity of a radicle increases by unity on the addition of $(SO^2)''$ and the elimination of H.

In reality, a biatomic group like $(SO^2)''$ can unite with any radicle without modifying its atomicity, if it be joined to it by one only of its centres of attraction. The union of the group $(SO^2)''$ with an organic radicle, therefore, does not modify the atomicity of the latter; but if afterwards the radicle which has fixed $(SO^2)''$, and whose atomicity has not varied, loses H, this elimination, according to the usual law, increases its atomicity by one. The following figures illustrate this reasoning:



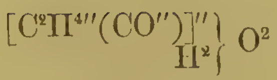
$(C^2H^3O)'$ Acetyl. $(SO^2)''$ Sulphuryl. H Hydrogen.



$(C^2H^2OSO^2)''$
Sulphacetyl.

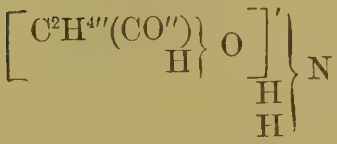
A perfect parallelism is observed between the sulpho-conjugate derivatives of this second class and certain substances which only differ from them by the substitution of carbonyl $(CO)''$ for sulphuryl $(SO^2)''$. The following table exhibits this:

| Series of the Carbonyl Radicle. | Series of the Sulphuryl Radicle. |
|---|---|
| $CO''$<br>Oxide of carbon. | $SO^{2''}$<br>Sulphurous anhydride. |
| $CO''O$<br>Carbonic anhydride. | $SO^{2''}O$<br>Sulphuric anhydride. |
| $CO''Cl^2$<br>Chloride of carbonyl. | $SO^{2''}Cl^2$<br>Chloride of sulphuryl. |
| $\left.\begin{matrix}[C^2H^5(CO'')]'\\ H\end{matrix}\right\}O$<br>Propionic acid. | $\left.\begin{matrix}[C^2H^5(SO^{2''})]'\\ H\end{matrix}\right\}O$<br>Ethyl-sulphurous acid. |
| $\left.\begin{matrix}[C^2H^5(CO'')]'\\ Cl\end{matrix}\right\}$<br>Chloride of propionyl. | $\left.\begin{matrix}[C^2H^5(SO^{2''})]''\\ Cl\end{matrix}\right\}$<br>Ethyl-sulphurous chloride. |



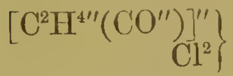
$\left.\begin{matrix}[C^2H^{4''}(CO'')]''\\ H^2\end{matrix}\right\}O^2$

Lactic acid.



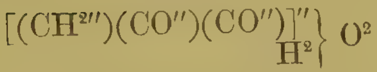
$\left.\begin{matrix}\left[\left.\begin{matrix}C^2H^{4''}(CO'')\\ H\end{matrix}\right\}O\right]'\\ H\\ H\end{matrix}\right\}N$

Lactic monamide (alanine).



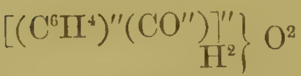
$\left.\begin{matrix}[C^2H^{4''}(CO'')]''\\ Cl^2\end{matrix}\right\}$

Chloride of lactyl.



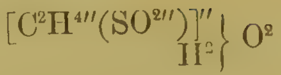
$\left.\begin{matrix}[(CH^{2''})(CO'')(CO'')]''\\ H^2\end{matrix}\right\}O^2$

Malonic acid.



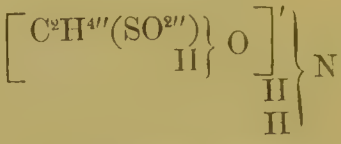
$\left.\begin{matrix}[(C^6H^4)''(CO'')]''\\ H^2\end{matrix}\right\}O^2$

Salicylic acid.



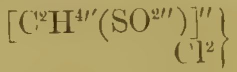
$\left.\begin{matrix}[C^2H^{4''}(SO^{2''})]''\\ H^2\end{matrix}\right\}O^2$

Isethionic acid.



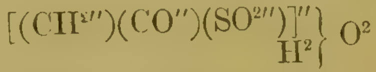
$\left.\begin{matrix}\left[\left.\begin{matrix}C^2H^{4''}(SO^{2''})\\ H\end{matrix}\right\}O\right]'\\ H\\ H\end{matrix}\right\}N$

Isethionic monamide (taurin).



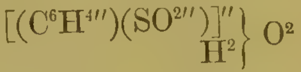
$\left.\begin{matrix}[C^2H^{4''}(SO^{2''})]''\\ Cl^2\end{matrix}\right\}$

Isethionic chloride.



$\left.\begin{matrix}[(CH^{2''})(CO'')(SO^{2''})]''\\ H^2\end{matrix}\right\}O^2$

Sulphacetic acid.



$\left.\begin{matrix}[(C^6H^{4''})(SO^{2''})]''\\ H^2\end{matrix}\right\}O^2$

Sulphophenic acid.

The analogies just shown exist not only in the formulæ, but also in the properties of the bodies spoken of, and even in the mode of their formation.

Thus, both lactic and isethionic acids are biatomic and monobasic.

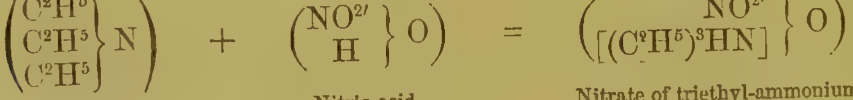
Malonic and sulphacetic acids are biatomic and bibasic.

Salicylic acid is obtained by the action of carbonic anhydride on the phenate of sodium; sulphophenic acid, by the action of sulphuric anhydride on phenol. (Phenol only differs from the phenate of sodium by having H substituted for Na).

It would be difficult to find among organic compounds analogies more clearly marked than these.

**Nitric Acid.**—Nitric acid is a powerful reagent, which few substances can resist. It may act in three different ways:

1st. It may combine directly with the organic substance; this is the case with the compound ammonias:



$$\left(\left.\begin{matrix}C^2H^5\\ C^2H^5\\ C^2H^5\end{matrix}\right\}N\right) + \left(\left.\begin{matrix}NO^{2'}\\ H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}NO^{2'}\\ [(C^2H^5)^3HN]\end{matrix}\right\}O\right)$$

Triethylamine. Nitric acid. Nitrate of triethyl-ammonium.

2nd. It may be decomposed and act as an oxidizing agent. This is its usual mode of action, especially when it is diluted with water.

3rd. It may act by double decomposition; under its influence organic substances lose hydrogen, for which the residue of the nitric acid is substituted:

$$\underset{\text{Benzine.}}{(C^6H^6)} + \underset{\text{Nitric acid.}}{(NHO^3)} = \underset{\text{Water.}}{(H^2O)} + \underset{\text{Nitro-benzine.}}{(C^6H^5(NO^2))}$$

Here, as with sulphuric acid, two cases may arise.

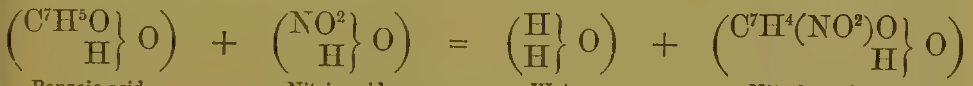
*First.*—The radicle of the organic substance may be substituted for the typical hydrogen of nitric acid. The product obtained then possesses an atomicity equal to 0, if the group substituted for H do not itself contain typical hydrogen, and an atomicity equal to 1, 2, 3 . . . *n*, if this group contain 1, 2, 3 . . . *n* atoms of typical hydrogen.

Thus the nitrate of ethyl $\left(\left.\begin{matrix}NO^2\\C^2H^5\end{matrix}\right\} O\right)$ is neutral, and the mononitric glycol $\left[\left.\begin{matrix} NO^{2\prime} \\ \left(\left.\begin{matrix}C^2H^{4\prime\prime}\\ H\end{matrix}\right\} O\right)^{\prime} \end{matrix}\right\} O^2\right]$ is monatomic, because the radicle ethyl $(C^2H^5)$ is neutral, while the residue of the glycol $\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\H\end{matrix}\right\} O\right)$ contains an atom of typical hydrogen.

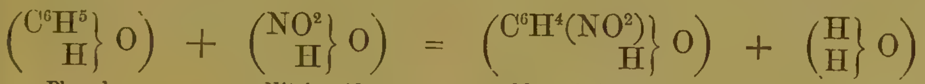
The atomicity of the nitrous products of this first class may be calculated by the formula we have given for the analogous sulpho-conjugate derivatives, making in this formula $b' = 1$ instead of $= 2$; we have then:

$$B = b^m + b'^n - 2n'.$$

*Second.*—The radicle $(NO^2)$ of nitric acid may be substituted for hydrogen of the radicle of the organic substance. In this case the atomicity remains the same as it was before the substitution. Like the analogous sulpho-conjugate compounds, it may also be calculated by means of the formula $B = b^m + b'^n - (m + n - 1)$, making $b' = 1$. We have examples of this kind of substitution in the production of nitrobenzoic acid, mononitric phenol, etc.:



$$\underset{\text{Benzoic acid.}}{\left(\left.\begin{matrix}C^7H^5O\\H\end{matrix}\right\} O\right)} + \underset{\text{Nitric acid.}}{\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\} O\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\} O\right)} + \underset{\text{Nitrobenzoic acid.}}{\left(\left.\begin{matrix}C^7H^4(NO^2)O\\H\end{matrix}\right\} O\right)},$$



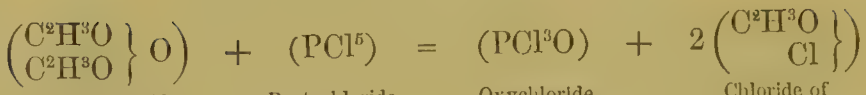
$$\underset{\text{Phenol.}}{\left(\left.\begin{matrix}C^6H^5\\H\end{matrix}\right\} O\right)} + \underset{\text{Nitric acid.}}{\left(\left.\begin{matrix}NO^2\\H\end{matrix}\right\} O\right)} = \underset{\text{Mononitric phenol.}}{\left(\left.\begin{matrix}C^6H^4(NO^2)\\H\end{matrix}\right\} O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\} O\right)}$$

Nitric acid has a special tendency to produce phenomena of substitution when it is concentrated. This tendency is increased by mixing it with sulphuric acid, probably because this always keeps it at the maximum of concentration by seizing the water which is formed.

**Chlorides of Phosphorus.**—The terchloride, oxychloride, and pentachloride of phosphorus furnish the means of substituting chlorine either for oxygen or for the group OH.

1st. They produce the substitution of chlorine for oxygen when they act on anhydrous oxides: according as the radicles of these oxides are even or uneven the molecule remains intact or is divided:

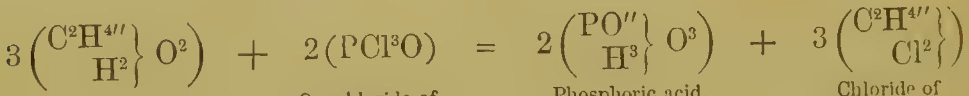
$$\underset{\text{Aldehyd.}}{(C^2H^4O)} + \underset{\substack{\text{Pentachloride}\\ \text{of phosphorus.}}}{(PCl^5)} = \underset{\substack{\text{Oxychloride}\\ \text{of phosphorus.}}}{(PCl^3O)} + \underset{\substack{\text{Chloride of}\\ \text{ethylidene.}}}{(C^2H^4Cl^2)}$$



$$\left(\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O\Big) + (PCl^5) = (PCl^3O) + 2\left(\begin{matrix}C^2H^3O\\Cl\end{matrix}\right\}\Big)$$

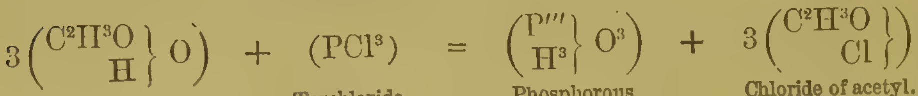
Acetic anhydride. Pentachloride of phosphorus. Oxychloride of phosphorus. Chloride of acetyl.

2nd. They give rise to the replacement of the group OH by chlorine when they act on hydrates:



$$3\left(\begin{matrix}C^2H^{4''}\\H^2\end{matrix}\right\}O^2\Big) + 2(PCl^3O) = 2\left(\begin{matrix}PO''\\H^3\end{matrix}\right\}O^3\Big) + 3\left(\begin{matrix}C^2H^{4''}\\Cl^2\end{matrix}\right\}\Big)$$

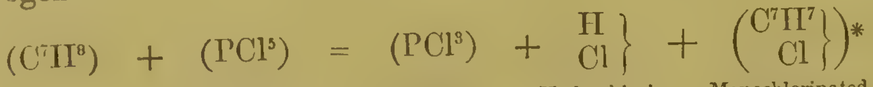
Glycol. Oxychloride of phosphorus. Phosphoric acid. Chloride of ethylene.



$$3\left(\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O\Big) + (PCl^3) = \left(\begin{matrix}P'''\\H^3\end{matrix}\right\}O^3\Big) + 3\left(\begin{matrix}C^2H^3O\\Cl\end{matrix}\right\}\Big)$$

Acetic acid. Terchloride of phosphorus. Phosphorous acid. Chloride of acetyl.

Besides the substituting action it possesses in common with the oxy- and ter-chlorides, the pentachloride of phosphorus also possesses a second action of substitution; it can be reduced to the state of terchloride, setting free chlorine, which becomes substituted for hydrogen:



$$(C^7H^8) + (PCl^5) = (PCl^3) + \begin{matrix}H\\Cl\end{matrix}\Big\} + \left(\begin{matrix}C^7H^7\\Cl\end{matrix}\right\}\Big)^*$$

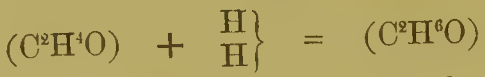
Toluene. Pentachloride of phosphorus. Terchloride of phosphorus. Hydrochloric acid. Monochlorinated toluene.

**Bromides and Iodides of Phosphorus.**—These bodies act exactly like the chlorides of phosphorus, of course with the exception that, instead of chlorine, it is bromine or iodine which they introduce into the organic molecules.

**Reducing Agents.**—By the designation reducing agents are indicated all those bodies whose action is the reverse of that of oxygen, chlorine, bromine, and iodine. At the head of these agents we place nascent hydrogen, obtained either by means of sodium amalgam and water, or by dissolving zinc in acids or alkalies. Then there are the bodies which are decomposed readily, yielding hydrogen, such as hydrosulphuric acid, and those which seize the oxygen of water, like sulphurous anhydride, the metals, especially potassium and sodium, etc.

Reducing agents can produce three orders of reactions:

1st. They may give rise to the fixing of hydrogen on an organic substance:



$$(C^2H^4O) + \begin{matrix}H\\H\end{matrix}\Big\} = (C^2H^6O)$$

Oxide of ethylene. Hydrogen. Alcohol.

2nd. They may remove the oxygen, chlorine, bromine, or iodine contained in a substance, without being substituted for them:

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* Naquet. Unpublished experiments.

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$$\underset{\text{Chloride of butyryl.}}{2\left(\left.\begin{matrix}C^4H^7O\\ Cl\end{matrix}\right\}\right)} + \underset{\text{Potassium.}}{\left.\begin{matrix}K\\ K\end{matrix}\right\}} = \underset{\text{Chloride of potassium.}}{2\left(\left.\begin{matrix}K\\ Cl\end{matrix}\right\}\right)} + \underset{\text{Butyryl.}}{\left(\left.\begin{matrix}C^4H^7O\\ C^4H^7O\end{matrix}\right\}\right)}$$

$$\underset{\text{Benzoic acid.}}{\left(\left.\begin{matrix}C^7H^5O\\ H\end{matrix}\right\}O\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\ H\end{matrix}\right\}} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)} + \underset{\text{Benzoic aldehyd.}}{\left(\left.\begin{matrix}C^7H^5O\\ H\end{matrix}\right\}\right)}$$

3rd. They may cause the substitution of hydrogen for oxygen, chlorine, bromine, or iodine. This is called inverse substitution. When hydrogen is substituted for oxygen, the substitution may take place by equivalent quantities:

$$\underset{\text{Benzoic acid.}}{\left(\left.\begin{matrix}C^7H^5O\\ H\end{matrix}\right\}O\right)} + \underset{\text{Hydrogen.}}{2\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}\right)} = \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)} + \underset{\text{Benzoic alcohol.}}{\left(\left.\begin{matrix}C^7H^7\\ H\end{matrix}\right\}O\right)}$$

But it may also happen that the quantity of hydrogen which enters into the molecule is only the half of that which should enter as an equivalent to the oxygen eliminated:

$$\underset{\text{Nitrobenzine.}}{[C^6H^5(NO^2)]} + \underset{\text{Hydrogen.}}{3\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}\right)} = \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)} + \underset{\text{Aniline.}}{\left(\left.\begin{matrix}C^6H^5\\ H\\ H\end{matrix}\right\}N\right)}$$

**Acid Sulphites of the Alkalies.**—These are used to purify aldehyds. With these bodies they form crystallizable compounds which are easily separated from the oils with which the aldehyds are often mixed, and which are decomposed under the influence of alkalies, leaving the aldehyd the elements of which they contain.

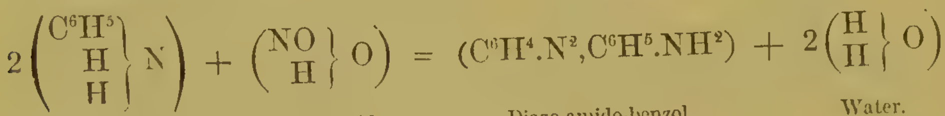
**Ammonia.**—Ammonia unites directly with acids, forming salts which are generally very soluble: it also unites with the anhydrides of polyatomic alcohols and of biatomic and monobasic acids. Moreover, it undergoes double decomposition with many aldehyds, with the anhydrides of acids whose basicity is equal to their atomicity, with the chlorides, bromides, and iodides of alcohol radicles, with compound ethers, etc. In all these cases nitrides are formed.

Certain colourless substances are known, apparently belonging to the class of phenols, which, under the simultaneous influence of oxygen and ammonia, give rise to nitrogenized colouring principles. Thus orcin is transformed into orcein.

**Nitrous Acid.**—Nitrous acid acts on the nitrides and transforms them into corresponding oxides:

$$\underset{\text{Acetamide.}}{\left(\left.\begin{matrix}C^2H^3O\\ H^2\end{matrix}\right\}N\right)} + \underset{\text{Nitrous acid.}}{\left(\left.\begin{matrix}NO'\\ H\end{matrix}\right\}O\right)} = \underset{\text{Nitrogen.}}{\left.\begin{matrix}N\\ N\end{matrix}\right\}} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)} + \underset{\text{Acetic acid.}}{\left(\left.\begin{matrix}C^2H^3O\\ H\end{matrix}\right\}O\right)}$$

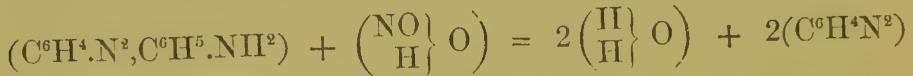
Nitrous acid, in alcoholic solution, gives rise to another kind of reaction: N is substituted for $H^3$. In this case, the product of substitution remains united to an unmodified molecule of the original compound:



$$2\left(\left.\begin{matrix}C^6H^5\\ H\\ H\end{matrix}\right\}N\right) + \left(\left.\begin{matrix}NO\\ H\end{matrix}\right\}O\right) = (C^6H^4.N^2,C^6H^5.NH^2) + 2\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right)$$

Aniline. Nitrous acid. Diazo-amido-benzol. Water.

If the action of nitrous acid be prolonged, the new compound also exchanges $H^3$ for N, and we have two molecules of a product which represents the primitive nitride in which N takes the place of $H^3$:

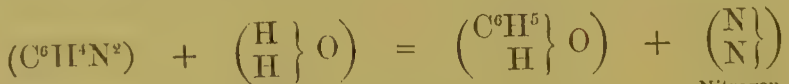


$$(C^6H^4.N^2,C^6H^5.NH^2) + \left(\left.\begin{matrix}NO\\ H\end{matrix}\right\}O\right) = 2\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right) + 2(C^6H^4N^2)$$

Diazo-amido-benzol. Nitrous acid. Water. Diazo-benzol.

Compounds analogous to diazo-benzol are readily produced when nitrous acid acts on a solution of an amidated organic substance in aqueous or alcoholic nitric acid. They are always obtained in the state of nitrate. (*See* PROPERTIES OF PRIMARY MONAMINES).

These products are transformed into hydrates disengaging nitrogen, when boiled with water:



$$(C^6H^4N^2) + \left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}C^6H^5\\ H\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}N\\ N\end{matrix}\right\}\right)$$

Diazo-benzol. Water. Phenol. Nitrogen.

**Dehydrating Agents.**—We have already seen that sulphuric acid is a dehydrating agent. Chloride of zinc and phosphoric anhydride act in the same manner, and are preferable to it. We shall not dwell on the mode of reaction of these bodies. They simply separate water from organic substances. Sometimes this elimination takes place at the cost of a single molecule, sometimes at that of several organic molecules:

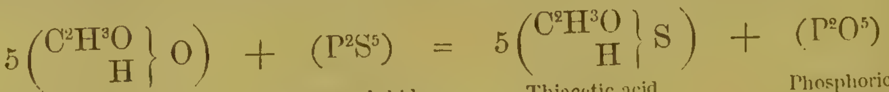
$$(C^2H^6O) = (C^2H^{4''}) + (H^2O)$$

Alcohol. Ethylene. Water.

$$2(C^2H^6O) = (C^4H^{10}O) + (H^2O)$$

Alcohol. Ether. Water.

**Sulphide of Phosphorus.**—M. Kékulé uses the sulphide of phosphorus in order to substitute sulphur for oxygen in acids and alcohols:



$$5\left(\left.\begin{matrix}C^2H^3O\\ H\end{matrix}\right\}O\right) + (P^2S^5) = 5\left(\left.\begin{matrix}C^2H^3O\\ H\end{matrix}\right\}S\right) + (P^2O^5)$$

Acetic acid. Pentasulphide of phosphorus. Thiacetic acid. Phosphoric anhydride.

**Potash and Soda.**—These bodies may be used in aqueous or in alcoholic solution, in a state of fusion, or in that of mixture with lime. Potash-lime possesses an advantage over potash in that it does not so readily attack vessels of glass or porcelain in which operations are conducted.

The reactions to which the caustic alkalies give rise are very numerous.

1st. They can combine directly with certain organic molecules: sometimes these molecules are acid anhydrides, and sometimes they are only non-saturated bodies. In any case a salt is produced from which an acid may be extracted which differs from the original body by the elements of water:

$$\underset{\text{Lactic anhydride.}}{(C^3H^4O^2)} + \underset{\text{Potassic hydrate.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic lactate.}}{(C^3H^5KO^3)}$$

$$\underset{\text{Oxide of carbon.}}{(CO'')} + \underset{\text{Potassic hydrate.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic formiate.}}{(CHKO^2)}$$

$$\underset{\text{Camphor.}}{(C^{10}H^{16}O)} + \underset{\text{Potassic hydrate.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic campholate.}}{(C^{10}H^{17}KO^2)}$$

2nd. They undergo double decomposition with acids: water is eliminated and a salt is formed:

$$\underset{\text{Acetic acid.}}{\left(\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O\right)} + \underset{\text{Potassic hydrate.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic acetate.}}{\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

3rd. They cause oxidation, disengaging hydrogen. This reaction is a double decomposition, in which the organic substance and the alkali unite, losing hydrogen instead of water:

$$\underset{\text{Aldehyd.}}{\left(\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic acetate.}}{\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}}$$

$$\underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic acetate.}}{\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right)} + \underset{\text{Hydrogen.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}\right)}$$

4th. They transform the organic matter on which they act into an isomeric compound. In this manner, under their influence, furfuramide is converted into furfurine, and hydro-benzamide into amarine.

5th. They cause hydration and a subsequent double decomposition. Thus nitriles and amides fix water, and the ammoniacal salt produced is transformed into ammonia and an alkaline salt by double decomposition:

$$\underset{\text{Acetamide.}}{\left(\left.\begin{matrix}C^2H^3O\\H^2\end{matrix}\right\}N\right)} + \underset{\text{Potassic hydrate.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Ammonium.}}{(NH^3)} + \underset{\text{Potassic acetate.}}{\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right)}$$

6th. From those bodies which contain chlorine of addition, they remove half that chlorine, and it may be eliminated without taking hydrogen with it. The alkalies act in the same manner on brominated or iodized compounds:

$$\underset{\text{Chloride of ethylene.}}{(C^2H^4Cl^2)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Chlorinated ethylene.}}{(C^2H^3Cl)} + \underset{\text{Potassic chloride.}}{\left.\begin{matrix}K\\Cl\end{matrix}\right\}} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

$$\underset{\text{Bromide of bibrominated ethylene.}}{(C^2H^2Br^4)} + 3\underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = 3\underset{\text{Bromide of potassium.}}{\left(\left.\begin{matrix}K\\Br\end{matrix}\right\}\right)} + 2\underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Brominated acetylene.}}{(C^2HBr)}$$

For these reactions the alkalies require to be in alcoholic solution.

7th. Potash or soda do not always act on brominated or chlorinated compounds of substitution. Sometimes they exercise an action identical with the preceding, and they can also cause the substitution of OH, or if alcoholic solutions be used, of $(C^2H^5O)$ for Cl:

$$\underset{\text{Chloride of amyl (chlorinated hydride of amyl).}}{(C^5H^{11}Cl)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic chloride.}}{\left.\begin{matrix}K\\Cl\end{matrix}\right\}} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Amylene.}}{(C^5H^{10})}$$

$$\underset{\text{Brominated ethylene.}}{(C^2H^3Br)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic bromide.}}{\left.\begin{matrix}K\\Br\end{matrix}\right\}} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} + \underset{\text{Acetylene.}}{(C^2H^2)}$$

$$\underset{\text{Potassic chloracetate.}}{\left(\left.\begin{matrix}C^2H^2ClO\\K\end{matrix}\right\}O\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic glycolate.}}{\left(\left.\begin{matrix}C^2H^2O''\\HK\end{matrix}\right\}O^2\right)} + \underset{\text{Potassic chloride.}}{\left.\begin{matrix}K\\Cl\end{matrix}\right\}}$$

$$\underset{\text{Chlorinated chloride of benzoyl.}}{\left(\left.\begin{matrix}C^7H^6Cl\\Cl\end{matrix}\right\}\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} + \underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)} = \underset{\text{Chlorinated oxide of ethyl and benzoyl.}}{\left(\left.\begin{matrix}C^7H^6Cl\\C^2H^5\end{matrix}\right\}O\right)}$$

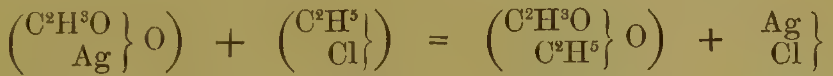
$$+ \underset{\text{Potassic chloride.}}{\left.\begin{matrix}K\\Cl\end{matrix}\right\}} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)}$$

This latter mode of reaction is produced more easily if ethylate of sodium $\left(\left.\begin{matrix}C^2H^5\\Na\end{matrix}\right\}O\right)$, obtained by dissolving sodium in alcohol, be substituted for potash.

**Oxide of Silver.**—The oxide of silver sometimes acts as an oxidizing agent, and is itself reduced to the metallic state.

In presence of water it acts on chlorinated substances in the same manner as potash does, that is to say, it removes hydrochloric acid from them, or it causes the replacement of Cl by OH.

**Acetate of Potassium or of Silver.**—These salts enter into double decomposition with chlorinated, brominated, or iodized compounds, and give rise to the replacement of halogen metalloids by the halogen residue of acetic acid ($C^2H^3O,O$):



$$\left(\left.\begin{matrix}C^2H^3O\\ Ag\end{matrix}\right\} O\right) + \left(\left.\begin{matrix}C^2H^5\\ Cl\end{matrix}\right\}\right) = \left(\left.\begin{matrix}C^2H^3O\\ C^2H^5\end{matrix}\right\} O\right) + \left.\begin{matrix}Ag\\ Cl\end{matrix}\right\}$$

Acetate of silver. Chloride of ethyl. Acetate of ethyl. Chloride of silver.

## RELATIONS BETWEEN THE PHYSICAL PROPERTIES AND THE COMPOSITION OF ORGANIC SUBSTANCES.

It is to be expected that all the physical properties of bodies should bear some relation to their composition. Those properties in which certain relations of this kind have been proved are:

The crystalline form, the point of fusion, the boiling point, the index of refraction, the specific heat, and the density in the liquid state.

**Crystalline Form.**—The phenomena of isomorphism are often observed between a given body and its chlorinated, brominated, or nitrous derivatives. These phenomena are not always observed, but it is possible that this may be owing to isomerism. The derivatives of naphthalin each exist under several isomeric modifications, the respective terms of which are isomorphous. These derivatives may be classed in three series:

1st. A series $\alpha$, in which the crystals assume the form of six-sided prisms of 120°, are soft, cleave parallel to their axis, and dissolve readily in ether, but sparingly in alcohol.

2nd. A series $\beta$, in which the three sides of the prism are almost equally inclined towards each other (100–103°).

3rd. A series $\gamma$, in which the naphthalic derivatives crystallize in prisms of the rhombic system (112–113°), which form small elastic needles.

Many cases of isomorphism are found among the nitrous derivatives. Thus binitrous, trinitrous, and pentanitrous phenol all crystallize in the same manner. When bodies are both isomeric and isomorphous, they are called isomeromorphous. In order to understand these compounds, let us take a molecule of naphthalin $C^{10}H^4H^2H^2$. If $Cl^2$ be substituted for $H^2$, we have $C^{10}H^4H^2Cl^2$. Then, if $Br^2$ be substituted for $H^2$, the compound $C^{10}H^4Br^2Cl^2$ is obtained. If, instead of commencing with chlorine, bromine were used, the body $C^{10}H^4Cl^2Br^2$ would be formed.

These two bodies are isomeric, as bromine and chlorine do not replace the same atoms of hydrogen, and they are isomorphous, because the atoms are similarly arranged; they are *isomeromorphous.*

Bodies are said to be paramorphous when they crystallize in similar forms, but in different systems, such as the tetrachloride of naphthalin $C^{10}H^8Cl^4$, and the tetrachloride of chlorinated naphthalin $C^{10}H^7ClCl^4$.

Those bodies are called hemimorphous which are very similar in their chemical composition and functions, and crystallize in forms of which several angles are alike and others very different, whether these forms belong to the same system or not. Such are: the formiate of barium $\left(\left.\begin{matrix}(CHO)^2\\ Ba''\end{matrix}\right\}O^2\right)$, the propionate of barium $\left(\left.\begin{matrix}(C^3H^5O)^2\\ Ba''\end{matrix}\right\}O^2+aq.\right)$, and the acetate of barium $\left(\left.\begin{matrix}(C^2H^3O)^2\\ Ba''\end{matrix}\right\}O^2+aq.\right)$.

M. Gaudin has recently published several communications in which he professes to be able to deduce the arrangement of their atoms from the crystalline forms of bodies. But the forms this chemist is obliged to attribute to the molecules are not in conformity with the laws of atomicity. Until he can modify his theory, so as to bring it into accordance with these laws, it need not be taken into consideration.

**Point of Fusion.**—Homologous bodies have a fusing point which becomes higher the more their molecule is complicated. This rule is general with the fatty acids $C^nH^{2n}O^2$. It has also been observed that, in the chloro-conjugate or bromo-conjugate derivatives, the point of fusion rises with the number of atoms of chlorine or bromine which enter into the molecule. But in order that this latter law be verified, only those derivatives of a body which are isomorphous must be compared, and their isomerism must be taken into account.

Thus, in the three series of naphthalin derivatives, we have, according to Laurent:

| | Fusing point. |
|---|---|
| Series α. | |
| $C^{10}H^6Cl^2$ | liquid |
| $C^{10}H^5Cl^3$ | 75° |
| $C^{10}H^5BrCl^2$ | 80° |
| $C^{10}H^4Cl^4$ | 106° |
| $C^{10}H^4BrCl^3$ | 110° |
| $C^{10}H^2BrCl^5$ | 143° |
| Series β. | |
| $C^{10}H^6Cl^2$ | 50° |
| $C^{10}H^6Br^2$ | 59° |
| $C^{10}H^5Cl^3$ | 79° |
| $C^{10}Cl^8$ | 172° |
| Series γ. | |
| $C^{10}H^4Cl^4$ | 123° |
| $C^{10}H^4Br^2Cl^2$ | 166° |
| $C^{10}H^3BrCl^4$ | 165–168° |

The compounds of the preceding bodies with chlorine have no regular fusing point, but it is remarkable that when melted they solidify, sometimes at one temperature, sometimes at another, and they assume different crystalline forms according to the temperature at which they are solidified.

**Boiling Point.**—By examining the boiling points of a great number of homologous bodies, M. Kopp has discovered the following laws:

1st. Homologous bodies have boiling points which increase or diminish by 19° for each addition or subtraction of $CH^2$. Thus, methylic alcohol $CH^4O$ boils at 19° lower than vinic alcohol $C^2H^6O$.

2nd. The boiling point of an acid is 40° above that of the alcohol from which it is derived by oxidation.

3rd. A compound ether boils 82° below the acid which has the same formula; thus, the acetate of methyl boils 82° lower than propionic acid.

From this we deduce that a methylic ether boils at 63° lower, an ethylic ether at 44° lower, and an amylic ether at 13° higher than the corresponding acid.

Moreover, Gerhardt states that each atom of carbon raises the boiling point 35°, and that each double atom of hydrogen lowers it 15°, which for $CH^2$ would give a difference of 20°. Kopp thinks that each atom of carbon raises the boiling point 29°, and that each double atom of hydrogen lowers it 10°, which would give the difference of 19° for $CH^2$.

M. Chancel, remarking that boiling points calculated according to Kopp's law are generally too high, has proposed to substitute for this law that expressed by the following formula:

$$E = C + (n19) - 0{\cdot}5n^2.$$

E is the boiling point of a compound, C that of the first term of the series, and $n$ represents the number of the order of the compound in this series.

M. Kopp's laws are far from being accurate in all cases. It is known that the difference is greater than 19° for $CH^2$ in the homologues of oxide of ethyl and in those of benzine, and that it is less than this number in the homologues of acetic anhydride; but M. Wurtz has discovered a still more remarkable exception. In the glycol series, the boiling point decreases from the first term, ordinary glycol $C^2H^6O^2$, to the fourth term, amyl-glycol $C^5H^{12}O^2$. Beyond amyl-glycol the boiling point rises with the molecular complication.

These differences may be owing to several causes. One of the chief is isomerism, because two isomeric bodies often boil at very different temperatures. Perhaps such bodies, though considered as homologous, are only isomers of their respective homologues.

M. Regnault has found that, if the boiling points of different homologous bodies be taken under different pressures, the curves of the boiling points which are obtained are not parallel. It is therefore possible that in each series there may be constant differences between the boiling points of homologous bodies, but that these differences only exist under certain pressures which may vary from one series to another. It may even be supposed that the variations the pressure undergoes on changing the series, in order to obtain constant differences in the boiling points, themselves follow a determined law which may one day be discovered.

M. Berthelot, in his "Organic Chemistry," adds the following remarks to M. Kopp's laws:

1st. When several bodies are formed in an analogous manner by the action of a compound on several different substances, an almost identical difference is observed between the boiling points of these bodies and those of the substances whence they are derived; which may be expressed by the formula $E-e=F-f\pm a$, calling E and F two generators of the bodies $e$ and $f$, and $a$ being a constant. Thus:

| | | Difference. |
|---|---|---|
| Alcohol $C^2H^6O$ boils at | 78° | 67°. |
| Hydrochloric ether $C^2H^6O+HCl-H^2O$ boils at | 11° | |
| Acetic acid $C^2H^4O^2$ boils at | 117° | 62°. |
| Chloride of acetyl $C^2H^4O^2+HCl-H^2O$ boils at | 55° | |
| Alcohol $C^2H^6O$ boils at | 78° | 42° |
| Ether $C^2H^6O+C^2H^6O-H^2O$ boils at | 36° | |
| Allylic alcohol $C^3H^6O$ boils at | 103° | 40°·5 |
| Allyl-ethylic ether $C^2H^6O+C^3H^6O-H^2O$ boils at | 62·5 | |

2nd. When a molecule of water is removed from or added to an organic compound, its boiling point is lowered or raised 100° or 110°.

Amylic alcohol $C^5H^{12}O$ boils at 132°; amylene $C^5H^{10}$ boils at 35°: difference 97°.

From this and the preceding rule we deduce that the fixation of HCl raises the boiling point about 44°, and the fixation of HBr, 73°. In reality, the fixation of $H^2O$ would raise the boiling point 110°; but on substituting a molecule of hydrochloric acid for a molecule of water in the oxygenized body produced, its boiling point would be lowered 66°; the chlorinated compound would therefore differ from the original compound by 110 − 66, or 44°. So 73° are calculated for the addition of HBr, on the supposition that the substitution of HBr for $H^2O$ lowers the boiling point 37°.

3rd. The lowering of the boiling point in consequence of the elimination of $H^2O$ applies to the compounds formed by the union of two distinct principles. In order to find the boiling point F of these latter compounds, knowing those E and $f$ of their generators, we have the formula: $E+f-120=F$.

| | |
|---|---|
| Acetic acid boils at | $117° = E$ |
| Alcohol boils at | $78° = f$ |
| $E+f=$ | 195° |
| Acetic ether boils at | $74° = F$ |
| Diference between $E+f-F=$ | 121° |

4th. In a more general way, the boiling point of a complex body is plainly equal to the sum of the boiling points of the generating bodies, less that of the bodies eliminated.

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From the formula:

$$E - e = F - f \pm a$$

we get:

$$E + f - e = F \pm a$$

The preceding laws are far from being generally applicable to all bodies in organic chemistry. This may be proved by representing the boiling points of the homologous series graphically in the following manner:

Let the exponents $n$ of the carbon be taken for abscissæ, and the boiling points $t$ of the different homologous bodies for which this exponent is 1, 2, 3, etc. for ordinates; let the points thus determined be joined by a continuous line, and we shall have a line which will render manifest the relations which exist between $n$ and $t$. The line will be straight, or nearly so, for alcohols, the fatty acids and their ethers, and curved for the carbides of hydrogen $C^nH^{2n}$, as Favre and Silbermann have remarked, and for the carbides $C^nH^{2n+2}$.

The line which joins the boiling points of butylene, amylene, hexylene, œnanthylene, and caprylene, is not very regular, owing to the different sources from whence these products are extracted, and consequently to the possibility of their being isomers. It is not so with the curve of the polymers of amylene, compounds evidently of similar constitution: this curve is represented in the interval found by the equation: $t = 140 + 41n - 1{\cdot}3n^2 + 0{\cdot}02n^3$.

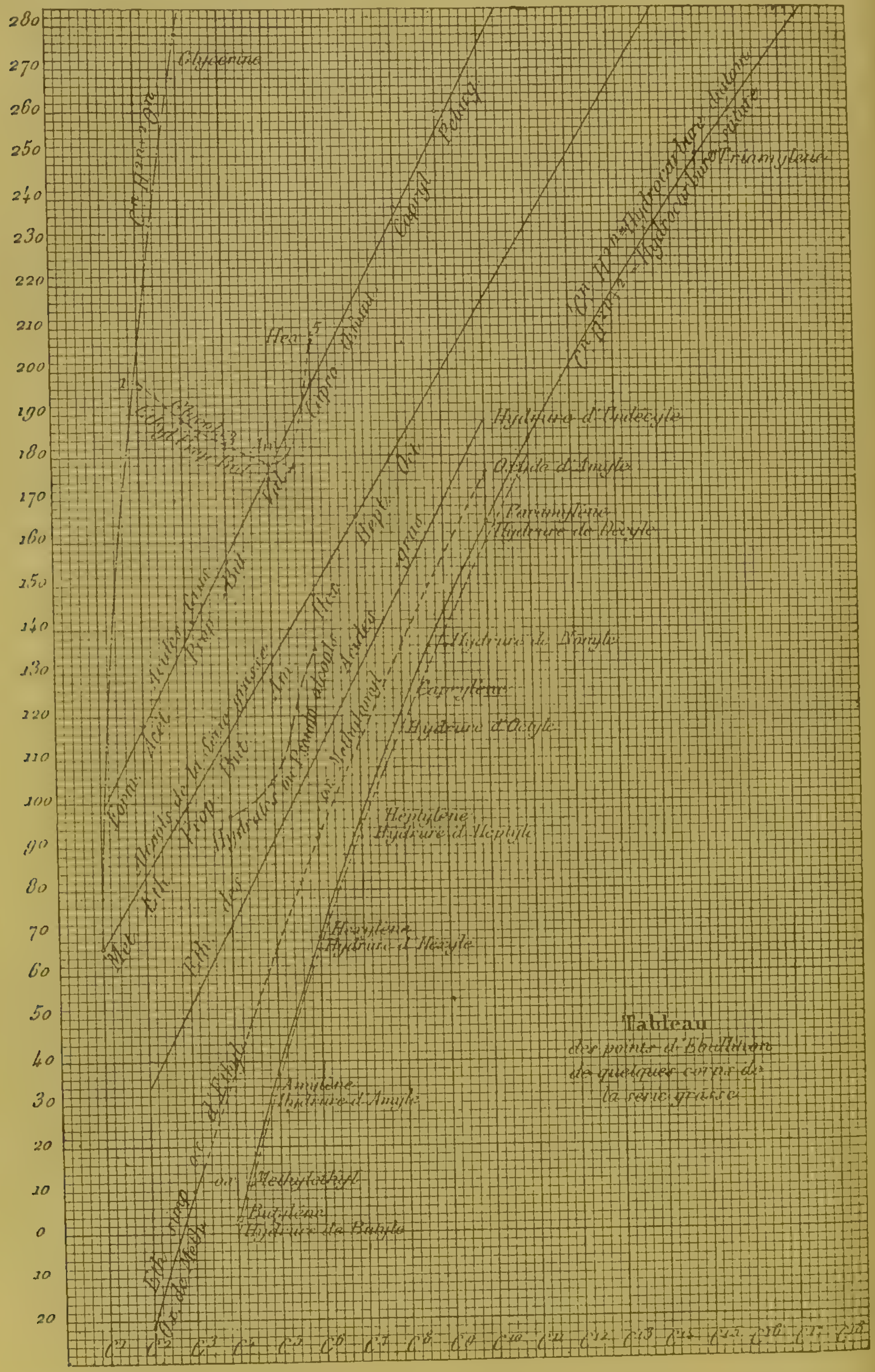
The curve of the hydrides of American petroleum $C^nH^{2n+2}$ is blended with the preceding line in its higher terms.

A remarkable inflection is observed in the line of the glycols; amylenic glycol constitutes a well-marked minimum; the curve of the hydrates of the carbides $C^nH^{2n}$ presents the same peculiarity, and the hydrate of amylene is the furthest removed, by its boiling point, from the isomeric alcohol.

The same mode of representation is applicable to series which are not homologous, to the series $C^nH^{2n+2}O^n$ for instance, which comprises wood-spirit, glycol and glycerine, alcohols whose atomicity is expressed by the exponent of the carbon which they contain.

The curve corresponding to this series is still undetermined, owing to the uncertainty existing on the subject of the boiling point of glycerine; but it clearly indicates that erythrite should boil (a theoretical deduction from its decomposition) at about 305°. On taking the boiling points 65, 197, 277, for the alcohols named above, we obtain by the equation $t = 119 + 210n - 26n^2$,—which represents the curve in its known parts,—the number 305.

The table on page 778 shows all the relations discovered between the boiling points of alcohols, their ethers, etc.: the explanations it gives will often be found useful.*



**Specific Heats.**—We said, in the early part of this work, that in a solid molecule the different simple atoms retain their specific heats. As since the specific heat given for each simple atom is 6·666, the product of the weight of a molecule P, multiplied by its specific heat C, will give *n* 6·666; *n* being the number of atoms of which it is composed.

---

* This table of boiling points has been constructed by M. Salet.

Knowing the formula of a body, we may ascertain the number *n* 6·666, which represents its molecular heat, and on dividing this number by the molecular weight, we obtain the specific heat of the substance.

However, by this means only an approximation to the true specific heat can be obtained; and, besides, Woestyn's law does not apply to all bodies.*

**Heat of Combustion.**—MM. Favre and Silbermann have determined the heat of combustion of a great number of organic substances; but until lately no attempt has been made to apply the results of these researches to a theory of thermo-chemistry.

M. Berthelot has recently supplied this deficiency by publishing some researches in thermo-chemistry which greatly increase the interest attached to the experiments of these chemists. The following is a summary of his views:

Starting from the hypothesis that in the case of chemical compounds the atoms of bodies which enter into combination are precipitated upon each other very sharply, and that the heat disengaged in these combinations is owing to their collision, M. Berthelot thinks he can apply the principles of the mechanical theory of heat to thermo-chemistry, for, on the above supposition, chemical reactions are reduced to very complicated mechanical phenomena. He therefore states, that just as in bringing a mechanical system from an initial to a final state, a certain amount of work is necessary independent of that by means of which the transformation is actually accomplished, so the following theorem may be stated as a general principle in thermo-chemistry: "When a system of simple or compound bodies undergoes chemical or physical changes, which cause it to pass to another state without producing mechanical effects external to the system, the quantity of heat disengaged or absorbed entirely depends on the initial and final states of the system, whatever may be the order and character of the intermediate states." This is the theory of the calorific equivalent of chemical transformations.

In order to establish his theorem, M. Berthelot assumes, *à priori*, the equivalence between the quantity of heat disengaged or absorbed in a chemical transformation, and the amount of molecular actions necessary to produce it.

He thence deduces that:

---

* It may here be remarked that M. Kopp has shown by recent experiments that the variation in the specific heats of carbon, boron, and silicon (see page 25), in their different allotropic states, is not sufficient to account for the fact that the real atomic weights of these bodies do not correspond to those deduced from their atomic heats.—Tr.

1st. The heat disengaged in the decomposition of a body is equal to that absorbed in its formation, provided that the initial and final states be identical.

2nd. The quantity of heat disengaged in a series of transformations equals the sum of the quantities disengaged in each transformation, if the bodies finally produced be identical.

3rd. The difference between the quantity of heat disengaged in two series of transformations, starting from two distinct states to arrive at the same final state, is equal to that disengaged or absorbed in passing from one of the initial states to the other.

4th. If a body *a* disengage heat in uniting with *b* to form *ab*, and if *ab* then yield *a* to a third body *c* to form *ac*, the quantity of heat disengaged in this reaction is less than that disengaged in the direct formation of the compound *ac*, by that of the quantity of heat disengaged in the combination of *ab*. In one case we start from the initial state *ab* to arrive at *ac*, and in the other from the state *a* and the state *c* to arrive at *ac*: consequently, in conformity with the third principle, the quantity of heat should be less by that necessary to produce the initial state *ab*.

M. Berthelot has studied these phenomena. The heat of combination should be in ratio to the external mechanical effects produced in the reaction; for instance, it should be different in four cases which he cites:

1st. Two gases exposed to the atmospheric pressure are mixed in a reservoir in which they combine without exploding.

2nd. The combination takes place with explosion.

3rd. The combination is made in a receiver in which the gases are submitted to pressure, but without explosion.

4th. The gases may be mixed, subjected to pressure, and thrown into the atmosphere, the gaseous jet being ignited.

The first is the normal condition, there is no external work produced, and the heat disengaged corresponds to the force of the chemical combination of the two gases, and represents it. In the case of the explosion, there is a mechanical effect, and consequently heat absorbed, and the total heat disengaged is less than in the first case. According to theoretical considerations, the third case should give the same heat as the first. In the fourth case, the powerful force of the jet of gas compressed and thrown into the atmosphere is destroyed, that is to say, is transformed into heat which should be added to the heat of combination properly so called: this effect may, however, be compensated, for the molecules of the gases communicate their force to the molecules of the air, which causes an expenditure of force.

It is under these latter conditions that the heat of combustion of gases has been determined, but the source of error indicated may be overlooked as the gases do not pass into the calorimeter very quickly. We may therefore say, that in all the experiments given below for the heat developed by the combination of gases, there has been no appreiable work to accompany this combination. After thus eliminating xternal work, M. Berthelot proceeds to consider the influence of emperature on the heat of combination. The quantity of heat disengaged in a combination varies with the temperature at which the combination takes place.

This variation is expressed by a formula which M. Berthelot explains n the following manner :

Let $Q_t$ be the heat disengaged, when the combination takes place at a emperature $t$.

Let U be the heat necessary to bring the initial system without chemial combination from $t$ to T : this heat is absorbed by the system. Let $Q_T$ be the heat of combination of the system previously heated to T, nd let V be the quantity of heat that would be disengaged if the prolucts of the reaction were restored without chemical change from T to $t$. The initial and final states being the same in both cases, that is to say when the combination has been directly effected at $t$, and when he system has been previously heated to T, and after reaction restored by cooling to $t$, we shall have :

$$Q_t = Q_T - U + V, \text{ thence } Q_T = Q_t + U - V$$

(U − V) represents the variation of the heat of combination, with the temperature.

But $U = u_1 + u_2 + u_3 \ldots$ which belong to each of the simple or compound bodies which form the initial system : so $V = v_1 + v_2 + v_3 + \ldots$ These equations are resolved into heat absorbed without change of state by the simple change of temperature, and heat absorbed with change of state. The first of these is obtained by multiplying the mean specific heat of each of these bodies by the corresponding intervals of temperature $t$, and by the weight of the body experimented on. The second term is composed of the molecular heats of fusion or vaporization (heats of fusion and vaporization multiplied by the molecular weight of each body). In the case in which the state of the bodies is not changed, the formula for the heat of combination is

$$Q_T = Q_t + [\Sigma c - \Sigma c_1](T - t).$$

$\Sigma c$ being the sum of the mean specific heats of the original body for the interval $t$ which is considered, and $\Sigma c_1$, the same amount for the final system. It is clear that, in this case, the heat of combination would increase with the temperature, when $\Sigma c$ exceeds $\Sigma c_1$.

In cases where the component bodies and the compound all possess the same solid liquid or gaseous state, for instance, $H^2$ and O forming $H^2O$ below 100°, amylene and water forming amylic alcohol, or S and Pb forming sulphide of lead, experiment shows that the sum of the specific heats of the components is often greater than that of the compound, and, consequently, the heat of combination increases for the space of $t$, under which this condition is realized.

If for a space of time, $t$ which does not correspond to any change of state, it happens that $\Sigma c_1$ scarcely differs from $\Sigma c$, and that the heat of combination be very great, the correction $[\Sigma c - \Sigma c_1]\ (T - t)$ may be omitted.

But this is not the case where there is a change of state; let $f_1, f_2 \ldots$, be the molecular heats of fusion of the bodies in the initial system; $f'_1 . f'_2 \ldots$, the corresponding values for the bodies in the final system; $\phi_1, \phi_2 \ldots$, the heats of vaporization of the bodies in the initial system; $\phi'_1, \phi'_2 \ldots$, the same value for the bodies in the final system; let $t_1, t_2, t_3 \ldots t_\alpha$ be the temperatures corresponding to these points of fusion and of vaporization classed in order increasing from $t$ to T.

Let $c$ and $c_1$ be the mean specific heats for the interval from $t$ to $t_1$, $c'$ and $c'_1$ for that of $t_1$ to $t_2$, $c(^\alpha)$ and $c_1(^\alpha)$ for that of $t_\alpha$ to T.

On introducing these into the original formula, the following form is given to U and V:

$$U = \Sigma c(t_1 - t) + \Sigma c'(t_2 - t_1) + \ldots + \Sigma c^\alpha (T - t\alpha) + \Sigma f + \Sigma \phi;$$

$$V = \Sigma c_1(t_1 - t) + \Sigma c'_1(t_2 - t_1) + \ldots + \Sigma c_1{}^\alpha (T - t\alpha) + \Sigma f' + \Sigma \phi';$$

and the general formula becomes:

$$Q_T = Q_t + (\Sigma c - \Sigma c_1)(t_1 - t) + \ldots + (\Sigma c^\alpha - \Sigma c_1{}^\alpha)(T - t_\alpha)$$
$$+ \Sigma f + \Sigma \phi - \Sigma f' - \Sigma \phi'.$$

The term $(\Sigma c - \Sigma c_1)(t_1 - t)$ may be overlooked when the heat of combination is very great, and when an approximation only is required: the simplified formula would in this case be, $Q_T = Qt + \Sigma f + \Sigma \phi - \Sigma f' - \Sigma \phi'$.

In some cases the molecular heat of fusion being much less than that of vaporization, may be neglected in comparison with this latter; it will only be necessary to take the heat of vaporization into account.

Here we find another simplification: M. Berthelot, basing his ideas on the figures given by M. Regnault, says that the heat necessary to convert a molecule of a great number of bodies into two volumes of vapour, varies between 6000 and 11,000 calories (units of heat), and that the number 8000 may be regarded as a mean. Taking this mean, the heat of combination is calculated at a higher temperature than that at which it was found by experiment, as an approximation to the reality, by the following formula: let $n$ and $n'$ be the numbers of the atoms of bodies in the initial and final systems which become gaseous, we have $Q_T = Q_t + (n - n')\ 8000$. When $n = n'$, $Q_T = Q_t$ the heats of combinations are equal at the different temperatures, which happens in the formation of alcohol by water and olefiant gas between 0° and 200°, $C^2H^4 + H^2O = C^2H^6O$.

In the first term, two volumes of water become gaseous between 0° and 200°; and in the second, two volumes of alcohol also become gaseous in passing from 0° and 200°; $n$ is therefore equal to $n'$, and the quantities of heat disengaged in this reaction will be the same at the different temperatures between 0° and 200°.

We therefore see that the heat disengaged in chemical combinations is not generally constant: it varies with the physical state of the bodies and the temperature; the quantity can only be compared when the bodies are in the same conditions. The heat of combination of gaseous Cl and H to form gaseous HCl, cannot be compared with that of I solid and H gaseous to form HI gaseous. Before making the comparison, the bodies must be brought to the conditions in which such a comparison is possible. M. Berthelot thinks this can be done by such an elevation of the temperature as will bring the bodies which enter into combination, and the product of this combination, to the state of pure gases. The molecular specific heat of simple gases of the formulæ $H^2$, $N^2$, $O^2$, is the same, viz., 6·85. The compound gases, approaching the state of perfect gases, also possess specific heats equal to the sum of those of the simple gases which compose them. Starting from the temperature at which it acquires a perfectly gaseous state, the molecular heat of the compound should become independent of the temperature equal to the sum of the molecular heats of the component gases, $\Sigma c = \Sigma c'_1$, and the general formula will become $Q_T = Q_t$, because in the formula $Q_T = Q_t + U - V$, U would be equal to V. M. Berthelot calls "atomic (molecular) heat of combination" the heat disengaged at the temperature at which the components and compounds may be considered as perfect gases, and at which this heat is independent of a fresh increase of temperature. It follows from what has been said, that the heat of combination disengaged or absorbed in a chemical reaction is reduced to two terms.

*α*. The molecular heat of combination arising from the single effect of chemical affinities brought into action under comparable conditions, that is to say, when the bodies are in the state of perfect gases.

*β*. The heat arising from changes of state, specific heat, or physical modifications of bodies. This second cause is the reason that the quantity of heat disengaged or absorbed in one and the same reaction varies according to circumstances.

It is evident that in order to compare the heat disengaged in chemical reactions the molecular heat of combination of the compounds must first be found; but, unfortunately, this heat can very seldom be determined, and represents an ideal definition whenever the bodies which enter into reaction cannot exist in the state of perfect gas without decomposition. There is another method of bringing the bodies which enter into reaction to a state admitting of comparison, which consists in producing such a decrease of temperature that all the bodies become solid; in this case the equation would become $Q_t = Q_T + (\Sigma c_1 - \Sigma c)(T - t)$, and it may be admitted as an approximation, in the case of considerable disengagement of heat, that the specific heats vary very little, and that therefore every time the bodies reacting are solid in the initial and final systems, the chemical reactions may be regarded as comparable. The comparisons would be exact if an absolute zero could be reached: this is a condition quite as important as that of bodies being perfectly gaseous, but impossible to be realized even approximately in our experiments.

But besides these cases in which the reactions may be compared in all the bodies, there are groups of bodies having analogous chemical functions which, in the case of analogous reactions taking place under the same conditions, give disengagements of heat which may be compared among themselves. The formation of soluble salts by means of soluble acids and bases is an instance of this: MM. Favre and Silbermann have shown that the quantities of heat differ very little in different acids and bases when they are dissolved in such a manner that a fresh quantity of water added to the solution produces no disengagement of heat: under these conditions of molecular separation, for instance, the differences between ammoniacal gas, caustic baryta, and potash, disappear, and the bodies thus dissolved are brought to states which are nearly comparable.

But the quantities of heat disengaged in the formation of salts thus dissolved is very different from the heat of molecular combination corresponding to their formation under ordinary conditions, and we really know nothing concerning the relation between these two quantities of heat. In his second essay, M. Berthelot applies the theoretical considerations we have thus briefly stated to the calculation of the quantities of heat disengaged in the formation of organic compounds. As the formation of organic bodies generally takes place too slowly for it to be possible to measure directly the quantity of heat disengaged in these reactions, indirect means must be used for this purpose. M. Berthelot explains by an example the method by which he calculated these quantities, using for this the heat of combustion found by the experiments of Dulong, Andrews, Favre, and Silbermann, which had hitherto remained without theoretical value. Let us suppose that we have to calculate the heat disengaged in the formation of marsh gas.

$C + H^4 = CH^4$. This quantity of heat may be calculated when the heat of combustion of carbon, of H, and of marsh gas is respectively known, which numbers are given by MM. Favre and Silbermann's experiments.

Let us take C, $H^4$, $O^4$ at 0°, and at the state at which we know these bodies. This system may be changed into $2(H^2O)$ and $CO^2$ in two different ways: *a.* C is combined directly with $O^2$, and $H^4$ with $O^2$, to form $CO^2$ and $2(H^2O)$. The heat of molecular combustion is easily calculated. Direct experiment gives this for unity of weight, and we multiply by the molecular weights of the bodies brought into reaction. We find that on this combustion, taking place at 0°, 232000 represents the heat disengaged. *b.* Marsh gas is formed with C and $H^4$, which is accompanied by a disengagement of a quantity of heat which cannot be measured directly on account of the conditions of the reaction, and which we will call $x$.

The gas $CH^4$ thus formed, we combine it with $O^4$ by the reaction $CH^4 + O^4 = CO^2 + 2(H^2O)$, and measure the heat disengaged in this combustion; it is equal to 210000. In both cases, we started from the same initial system C, $H^4$, $O^4$, to end in the same final system $CO^2 + 2(H^2O)$: the quantities of heat disengaged in the two reactions should therefore be equal among themselves. In the direct formation of $CO^2$ and $2(H^2O)$ it has been seen that 232000 represented the quantity; in the second case, $x$ amount of heat was disengaged at the time of the formation of $CH^4$, and 210000 is the calorific equivalent for the combustion of $CH^4$ to form $CO^2 + 2(H^2O)$. We therefore have $232000 = x + 210000$ and $x = 232000 - 210000 = 32000$ heat units.*

M. Berthelot formulates the law deduced from these considerations, which he used in all his calculations, by saying that the difference between the heat of combustion of two equivalent systems is equal to the quantity of heat disengaged or absorbed when one of the systems is transformed into the other. We will sum up the results M. Berthelot arrived at by the application of this law, without entering into details of the calculations.

In the case of the gradual oxidation of a body, with the formation of successive terms containing the same number of atoms of C, the quantities of heat disengaged are evidently in proportion to the number of atoms of O consumed. For the oxidation of $C^2H^6O$, and its successive transformation into aldehyd, acetic acid, and oxalic acid, the number of the calorific equivalent corresponding to the consumption of each O is about equal to 54000. For methylic alcohol it would be 50000.

In the homologous series, the quantities of heat disengaged by the fixation of $O^2$ increases as the equivalent rises.

The study of isomerism may gain much by the consideration of thermo-chemical phenomena. Every transformation of a body into an isomeric body is accompanied by an absorption or disengagement of heat; an example of this is seen in sulphur.

We may see, *à priori*, that the amount of work, negative as well as positive, necessary to transform a body into its isomers is equal to O only in exceptional cases, and that as a general rule a disengagement or else an absorption of heat is necessary. Some data M. Berthelot has collected on this subject confirm what he states. The heat of combustion of the hydrocarbides $C^{10}H^{16}$ would be for

| | |
|---|---|
| Oil of lemon . . . . . . | 1490000 |
| — of turpentine . . . . | 1475000 |
| Terebene . . . . . . . . . | 1450000 |

The two first hydrocarbides possess a rotatory power which the latter is without, and the absence of which entails a certain disengagement of heat corresponding to a molecular work which has caused this loss. This fact is confirmed by experiment: when terebene is acted on by sulphuric acid, it loses its rotatory power and disengages a considerable quantity of heat; however, this reaction is not very clear, for it is accompanied by the formation of polymeric products.

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* A unit of heat is the amount of heat necessary to raise a kilogramme of water from 0° to 1° centigrade.—Tr.

The polymers also present interesting phenomena. The transformation of a body into its polymer is accompanied by a disengagement of heat. This is found, for instance, when terebene is transformed into diterebene. It is remarked at the same time that the boiling point and the density increase, but that the specific heat remains unchanged.

The comparison of metameric bodies having different functions is very interesting. With methylic alcohol, formic acid can give two different isomeric compounds: methyl-formic ether and acetic acid; the first by direct union, and the second by means of the cyanide of methyl.

The heat of combustion of the formiate of methyl is equal to 252000, and that of acetic acid to 210000 heat units. M. Berthelot thence concludes that the transformation of the formiate of methyl into acetic acid would be accompanied by a disengagement of 42000 units of heat. But it is a recognized fact that a considerable disengagement of heat, accompanied by a change of physical properties, corresponds to a more intimate combination of the component elements. In reality, in the case in question, methyl-formic ether may be easily transformed into formic acid and methylic alcohol, while acetic acid presents a very much greater stability. M. Berthelot thence concludes that acetic acid is a first principle, and formic ether a secondary one, comprising under the first denomination the combinations more stable and intimate than those to which he applies the second. The same fact is observed in the formic ethers of all alcohols compared to the acids which are isomeric with them, as well as generally in the acids $C^nH^{2n}O$ compared to the isomeric ethers.

For instance, butyric acid in burning disengages 497000, and acetic ether 553000 units of heat.

| | |
|---|---|
| Caproic acid . . . . . . . . | 812000 |
| Methyl-valeric ether . . . . . . | 856000 |

Generally, the more stable the compound, the greater is the heat disengaged in its formation. The compound formed under these conditions has a density and a boiling point higher than that of its isomer.

M. Berthelot observes with reason that the reciprocal transformations of isomeric bodies belong to the most general notions of mechanical chemistry; heat is disengaged: 1st, when several molecules unite to form a polymer; 2nd, when a secondary compound is transformed into a primary one. Lastly, M. Berthelot applies the principles we have just enumerated to the study of the formation of the different series of organic bodies, which study is of very great interest, into which, however, the limits of this work do not allow us to follow him.

**Atomic Volume.**—The term atomic volume is applied to the quotient of the atomic weight of a body divided by its density. It is evident that if there were no space between the atoms, this would be the volume of the atom itself. In reality this is not the case, because bodies contain considerable interspaces; but as the space existing around atoms of the same nature is constant under the same conditions, the quotient spoken of also expresses a constant relation: it represents the portion of space occupied by a given atom, including the space which always surrounds that atom.

On this conception of the term it is easy to understand that one body should have different atomic volumes, according to the combinations into which it enters and the place it there occupies. It is perfectly conceivable that the atoms of oxygen, for instance, are more or less distant from each other and from the atoms of other bodies, according to the part the former act in the compounds.

Now that the words atom and molecule possess very distinct acceptations, it is also necessary to distinguish the atomic from the molecular volume; this latter being the quotient, not of the atomic weight, but of the molecular weight divided by the density.

In order to compare the molecular volumes of different compounds, it is necessary that the bodies should be taken in as nearly as possible the same conditions. When liquids are in question, they should be brought to temperatures at which they have the same tension of vapour, that is to say, to their boiling points.

To be able to determine the molecular volume of a liquid, it is therefore necessary to know: 1st, its boiling point; 2nd, its density at a low temperature; 3rd, its coefficient of dilatation, from the temperature at which its density has been ascertained to that at which the liquid boils.

Kopp has determined the molecular volumes of a great number of organic substances, bringing all to that of water $= \frac{18}{1} = 18$; he finds: 1st, that the molecular volumes of homologous compounds differing by $n(CH^2)$, differ from each other by $n$ times a constant term, which is equal, as a mean, to 22.

2nd. That the molecular volumes of isomeric compounds are identical (at least when these isomers may be derived from the same type).

3rd. That the replacement of $H^2$ by O does not appear to modify the molecular volume.

4th. That the substitution of C for $H^2$ in a compound does not cause any change in the molecular volume.

From the preceding data, M. Kopp has calculated the atomic volumes of oxygen, hydrogen, and carbon in compounds.

From the fact that the substitution of C for $H^2$ does not cause the molecular volume to vary, he draws the conclusion that C occupies the same space as $H^2$.

Knowing that the specific volume of $CH^2$ is 22, he thence concludes that the atomic volume of C is $\frac{22}{2} = 11$, and the atomic volume of H $\frac{22}{2+2} = 5{\cdot}5$.

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Then he sought the atomic volume of oxygen of substitution, comparing the molecular volume of an aldehyd or an acetone with that of the corresponding hydrocarbide. Thus, if from the molecular volume of aldehyd $\left(\left.\begin{matrix}C^2H^3O\\ H\end{matrix}\right\}\right)$ (56·0 – 56·9) that of ethylene ($C^2H^4$) (44) be deducted, there remains $56 - 44 = 12$ for the volume occupied by the oxygen.

On calculating the atomic volume of the oxygen of substitution in several bodies, he found the values vary between 12·0 and 12·9, and took the number 12·2 as a mean term.

In order to determine the atomic volume of typical oxygen, he subtracted 11, that is to say, the atomic volume of $H^2$ from the number 18·8, which represents the molecular volume of boiling water. The difference 7·8 represents the atomic volume of typical oxygen.

By means of these numbers, M. Kopp succeeds in calculating the molecular volume of an organic compound not nitrogenized $C^aH^b(O)^cO^d$, multiplying the exponents $a$, $b$, $c$, $d$, by the respective atomic volumes of the bodies to whose symbols they are attached. Thus we have: $a \times 11 + b \times 5{\cdot}5 + c \times 12{\cdot}2 + d \times 7{\cdot}8 = V$; V being the molecular volume of the compound.

$(O)^c$ represents the oxygen of substitution and $O^d$ the typical oxygen.

Gerhardt objects to this calculation that it has the fault of being arbitrary, one body possessing several rational formulæ: but if the rational formulæ of a body may be varied in order to explain its reactions clearly, it can only be that the oxygen of addition becomes oxygen of substitution and *vice versâ*. Now, at the present time, in a great number of bodies (acids and alcohols) we know how to distinguish oxygen of addition from oxygen of substitution.

In other bodies the distinction is less easy, but because M. Kopp's formula can only be applied to the best-known compounds, it is no reason why it should be rejected: on the contrary, it should be a reason why it should be used to determine what is or is not typical oxygen in those bodies in which this question is still undecided.

It is clear that, knowing the molecular volume of a body, its density may be thence deduced: in fact, if $V = \frac{P}{D}$, $D = \frac{P}{V}$, the molecular volume may be used to find the molecular weight: we have $V \times D = P$.

**Index of Refraction.**—Landolt* has determined, by very exact methods, the index of refraction and the density of a great number of bodies, relatively to three lines $\mu\alpha$, $\mu\beta$, and $\mu\gamma$ of the hydrogen spectrum; he has also calculated the values $\frac{n-1}{d}$ in which $n$ is the index of refraction, and $d$ the density taken at the same temperature as this index; $D\frac{n-1}{d}P$, in which P represents the molecular weight of the substance. He calls the value given by this latter equation refraction-equivalent. He uses the first in preference to that of Schrauff $\frac{n^2-1}{d}$, to which the name of refractive power has been given.*

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* Poggendorf's *Annalen*, cxxii., p. 545; and cxxiii., p. 595; and *Annalen der Chemie und Pharmacie*, iv. supplement, vol. i.

The substances on which he has operated are: water, formic, acetic, propionic, butyric, valeric, caproic, and œnanthylic acids; methylic, ethylic, propylic, butylic, and amylic alcohols; the acetate of methyl, formiate of ethyl, acetate of ethyl, butyrate of methyl, valerate of methyl, butyrate of ethyl, formiate of amyl, valerate of ethyl, acetate of amyl, valerate of amyl, aldehyd, valeral, acetone, oxide of ethyl, acetic anhydride, ethylenic glycol, diacetate of ethylene, glycerine, lactic acid, phenol, essential oil of bitter almonds, salycylic aldehyd, salicylate of methyl, benzoate of methyl, and benzoate of ethyl.

The first question Landolt considered was, "Does the grouping of atoms in molecules exercise an influence on the specific refractive energy, or does this latter depend entirely on the centesimal composition, or is it quite independent of the intimate constitution of the body?"

Beckerel, Cahours, Deville, and Delf had already discovered that metameric bodies, having very similar densities, also have indices of refraction which are almost equal. Schrauff went farther than this: he remarked that the absolute refractive power of metameric or polymeric bodies, calculated from the formula $\frac{n^2-1}{d}$, is the same in all bodies of the same group; whence he concluded that the centesimal composition alone excercised any influence on this refracting power. But after this, Dale and Gladstone found that for several bodies, isomers of the benzoic group, and for several polymeric hydrocarbides, corresponding to the general formula $nC^5H^4$, the values of $\frac{n-1}{d}$ were expressed by numbers which are sometimes identical, but often very different: they thence concluded, contrary to the opinion of the previously-mentioned authors, that, according to circumstances, isomerism sometimes does, and sometimes does not affect the specific refractive energy. However, their experiments were not sufficient to establish the conclusions deduced. The differences observed might arise from errors in observation or from impurities contained in the substances operated with.

In order to remove this latter source of error from his experiments, Landolt operated with substances obtained by different modes of preparation, and he always found that, when the purification was perfect, the differences observed between the values of the refractive power did not exceed 0·004.

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* The expressions commonly used in English for these formulæ are "specific refractive energy" for $\frac{n-1}{d}$; "absolute refractive power" for $\frac{n^2-1}{d}$; and "molecular refractive power" or "refraction-equivalent" for $\frac{n-1}{d}P$.—T. S.

The following table contains the result of his researches on metameric and polymeric bodies. P indicates the molecular weight.

### METAMERIC BODIES.

| Formulæ. | NAMES OF BODIES. | Density $= d$. | Index of refraction $\mu a = n$ | Specific refractive energy $\frac{\mu a - 1}{d}$ | Refraction-equivalent $\frac{\mu a - 1}{d} P$ |
|---|---|---|---|---|---|
| $C^3H^6O^2$<br>$P = 74$ | Propionic acid . . . . . | 0·9963 | 1·3846 | 0·3860 | 28·57 |
| | Acetate of methyl . . . . | 0·9053 | 1·3592 | 0·3967 | 29·36 |
| | Formiate of ethyl . . . . | 0·9078 | 1·3580 | 0·3944 | 29·18 |
| $C^4H^8O^2$<br>$P = 88$ | Butyric acid. . . . . . | 0·9610 | 1·3955 | 0·4116 | 36·22 |
| | Acetate of ethyl. . . . . | 0·9021 | 1·3707 | 0·4110 | 36·17 |
| $C^5H^{10}O^2$<br>$P = 102$ | Valeric acid . . . . . . | 0·9313 | 1·4022 | 0·4319 | 44·05 |
| | Butyrate of methyl . . . . | 0·8976 | 1·3869 | 0·4311 | 43·97 |
| $C^6H^{12}O^2$<br>$P = 116$ | Caproic acid. . . . . . | 0·9252 | 1·4116 | 0·4449 | 51·61 |
| | Valerate of methyl . . . . | 0·8809 | 1·3927 | 0·4458 | 51·71 |
| | Butyrate of ethyl . . . . | 0·8906 | 1·3940 | 0·4424 | 51·32 |
| | Formiate of amyl . . . . | 0·8816 | 1·3959 | 0·4491 | 52·09 |
| $C^7H^{14}O^2$<br>$P = 130$ | Œnanthylic acid . . . . | 0·9175 | 1·4192 | 0·4569 | 59·40 |
| | Valerate of ethyl . . . . | 0·8674 | 1·3950 | 0·4554 | 59·20 |
| | Acetate of amyl . . . . | 0·8574 | 1·4017 | 0·4685 | 60·90 |
| $C^4H^{10}O$<br>$P = 74$ | Butylic alcohol . . . . . | 0·8074 | 1·3940 | 0·4879 | 36·11 |
| | Oxide of ethyl . . . . . | 0·7166 | 1·3511 | 0·4900 | 36·26 |

### POLYMERIC BODIES.

| Formulæ. | NAMES OF BODIES. | Density $= d$. | Index of refraction $\mu a = n$ | Specific refractive energy $\frac{\mu a - 1}{d}$ | Refraction-equivalent $\frac{\mu a - 1}{d} P$ |
|---|---|---|---|---|---|
| $C^2H^4O = 44$ | Aldehyd . . . . . | 0·7810 | 1·3298 | 0·4222 | 18·58 |
| $C^4H^8O^2 = 88$ | Butyric acid . . . . | 0·9610 | 1·3955 | 0·4116 | 36·22 |
| $C^3H^6O = 58$ | Acetone . . . . . | 0·7931 | 1·3572 | 0·4503 | 26·12 |
| $C^6H^{12}O^2 = 116$ | Caproic acid . . . . | 0·9252 | 1·4116 | 0·4449 | 51·61 |
| $C^5H^{10}O = 86$ | Valeral . . . . . | 0·7995 | 1·3861 | 0·4830 | 41·54 |
| $C^{10}H^{20}O^2 = 172$ | Valerate of amyl . . . | 0·8581 | 1·4098 | 0·4775 | 82·14 |

It will be seen on inspecting this table, that metameric bodies, though presenting marked differences in their index of refraction $\mu a$, and in their density $d$, only differ very slightly in their specific refractive energy $\frac{n-1}{d}$, and in their refraction-equivalent $\frac{n-1}{d}$ P. But however slight these differences may be, they exceed those which might be attributed to simple errors of observation, and they exceed them in a marked degree when bodies are operated upon which are difficult to purify, like the compound ethers. The molecular grouping therefore exercises an influence on the specific refractive energy of bodies, but this influence is scarcely appreciable.

The density and index of refraction of polymeric bodies increase when the molecule becomes double, but the value $\frac{\mu a-1}{d}$ decreases a little under the same conditions; whence it results that the refraction-equivalents $\frac{\mu a-1}{d}$ P are not exact multiples of each other. Besides the observations on the preceding isomeric bodies, Landolt has made other experiments to determine the influence of the atomic structure on the specific refractive power.

Mixtures may be considered as not having any atomic structure, and some may be obtained which present the same centesimal composition as a given definite compound. In the homologous series these are easily prepared by mixing two terms of the series, the one above and the other below that whose composition is to be imitated. Thus on mixing:

| | | | | |
|---|---|---|---|---|
| One molecule of acetic acid | | with one molecule of butyric acid | | a mixture is obtained having the same composition as propionic acid |
| $C^2H^4O^2$ | + | $C^4H^8O^2$ | = | $2(C^3H^6O^2)$ |
| Two of ethyl-alcohol | | one of amyl-alcohol | | same composition as propyl-alcohol |
| $2(C^2H^6O)$ | + | $C^5H^{12}O$ | = | $3(C^3H^8O)$ |
| Three of methylic alcohol | | one of amyl-alcohol | | as ethyl-alcohol |
| $3(CH^4O)$ | + | $C^5H^{12}O$ | = | $4(C^2H^6O)$ |
| One of ethyl-alcohol | | two of amyl-alcohol | | as butyl-alcohol |
| $C^2H^6O$ | + | $2(C^5H^{12}O)$ | = | $3(C^4H^{10}O)$ |

Landolt has also prepared liquids which present the same centesimal composition as glycerine by mixing:

| | | | | |
|---|---|---|---|---|
| One molecule of propionic acid | | with one molecule of water | | Composition of glycerine. |
| $C^3H^6O^2$ | + | $H^2O$ | = | $C^3H^8O^3$ |
| One of ethyl-alcohol | | one of formic acid | | |
| $C^2H^6O$ | + | $CH^2O^2$ | = | $C^3H^8O^3$ |
| One of methyl-alcohol | | with one of acetic acid | | |
| $CH^4O$ | + | $C^2H^4O^2$ | = | $C^3H^8O^3$ |

On mixing equivalent quantities of essential oil of bitter almonds and formic acid, he obtained a liquid which has the same centesimal composition as the salicylate of methyl $C^8H^8O^3$.

The results of his reseaches will be found in the following table, in which $\mu a$, $\mu\beta$ and $\mu\gamma$ indicate the indices of refraction taken in comparison with the three lines of the hydrogen spectrum.

| Names of Bodies. | $d$ | $\mu a$ | $\mu\beta$ | $\mu\gamma$ | $\frac{\mu a-1}{d}$ | $P\frac{\mu a-1}{d}$ |
|---|---|---|---|---|---|---|
| 1 mol. of acetic acid . . | 1·0514 | 1·3699 | 1·3765 | 1·3802 | | |
| 1 mol. of butyric acid . | 0·9610 | 1·3955 | 1·4025 | 1·4065 | | |
| Mixture . . . . . | 0·9930 | 1·3851 | 1·3918 | 1·3956 | 0·3878 | 28·69 |
| Propionic acid . . . | 0·9963 | 1·3846 | 1·3913 | 1·3951 | 0·3860 | 28·57 |
| 3 mol. of methyl-alcohol | 0·7964 | 1·3279 | 1·3332 | 1·3362 | | |
| 1 mol. of amyl-alcohol . | 0·8135 | 1·4057 | 1·4128 | 1·4169 | | |
| Mixture . . . . . | 0·8038 | 1·3640 | 1·3700 | 1·3735 | 0·4528 | 20·83 |
| Ethyl-alcohol. . . . | 0·8011 | 1·3605 | 1·3667 | 1·3700 | 0·4501 | 20·70 |
| 2 mol. of ethyl-alcohol . | 0·8011 | 1·3605 | 1·3667 | 1·3700 | | |
| 1 mol. of amyl-alcohol . | 0·8135 | 1·4057 | 1·4128 | 1·4169 | | |
| Mixture . . . . . | 0·8065 | 1·3822 | 1·3887 | 1·3925 | 0·4738 | 28·43 |
| Propyl-alcohol . . . | 0·8042 | 1·3794 | 1·3858 | 1·3893 | 0·4717 | 28·30 |
| 1 mol. of ethyl-alcohol . | 0·8011 | 1·3605 | 1·3667 | 1·3700 | | |
| 2 mol. of amyl-alcohol . | 0·8135 | 1·4057 | 1·4128 | 1·4169 | | |
| Mixture . . . . . | 0·8104 | 1·3961 | 1·4028 | 1·4068 | 0·4887 | 36·17 |
| Butyl-alcohol. . . . | 0·8074 | 1·3940 | 1·4007 | 1·4045 | 0·4879 | 36·11 |
| 1 mol. of propionic acid . | 0·9963 | 1·3846 | 1·3913 | 1·3951 | | |
| 1 mol. of water . . . | 1·0000 | 1·3311 | 1·3371 | 1·3404 | | |
| Mixture . . . . . | 1·0220 | 1·3856 | 1·3925 | 1·3964 | 0·3773 | 34·71 |
| 1 mol. of ethyl-alcohol . | 0·8011 | 1·3605 | 1·3667 | 1·3700 | | |
| 1 mol. of formic acid. . | 1·2211 | 1·3693 | 1·3764 | 1·3804 | | |
| Mixture . . . . . | 0·9602 | 1·3610 | 1·3675 | 1·3710 | 0·3760 | 34·59 |
| 1 mol. of methyl-alcohol | 0·7964 | 1·3279 | 1·3332 | 1·3362 | | |
| 1 mol. of acetic acid . . | 1·0514 | 1·3699 | 1·3765 | 1·3802 | | |
| Mixture . . . . . | 0·9606 | 1·3594 | 1·3656 | 1·3692 | 0·3741 | 34·42 |
| Glycerine. . . . . | 1·2615 | 1·4706 | 1·4785 | 1·4828 | 0·3731 | 34·32 |
| 1 mol. of benzoic aldehyde | 1·0474 | 1·5391 | 1·5624 | 1·5775 | | |
| 1 mol. of formic acid. . | 1·2211 | 1·3693 | 1·3764 | 1·3804 | | |
| Mixture . . . . . . | 1·0876 | 1·4900 | 1·5089 | 1·5210 | 0·4505 | 68·48 |
| Salicylate of methyl . | 1·1824 | 1·5302 | 1·5521 | 1·5672 | 0·4484 | 68·16 |

This table shows that the specific refractive energy $\frac{n-1}{d}$ and the refraction-equivalent $\frac{n^2-1}{d}$ P are about the same for definite compounds and for mixtures of the same composition. However, the value $\frac{n-1}{d}$ is a little more for mixtures than for the compounds. There is not a complete identity, but only a great approximation between them. Here, therefore, as in the study of isomeric bodies, we arrive at the conclusion that molecular structure exercises an influence, but a very small one, on the specific refractive energy.

### *Homologous Series.*

Berthelot was the first to study the modification the absolute refractive power $\left(\frac{n^2-1}{d}\right)$ undergoes, when we pass from one term to another in a homologous series. His experiments were not very numerous, but he arrived at the conclusion that bodies which differ by $n\text{CH}^2$ give a difference of $n18$ in the value $\frac{\text{P}n^2-1}{d}$. Schrauff has tried to prove, from the observations of Delfs, that in the series $\text{C}^n\text{H}^{2n}\text{O}^2$ the refraction-equivalent $\frac{\text{P}n^2-1}{d}$ of any term whatever is equal to the mean of the refraction-equivalents of two terms equally distant from this mean term, one above, the other below, and that consequently, in homologous series, the optical properties vary serially. Dale and Gladstone, who have also studied this question, have contented themselves with showing that the value $\frac{n-1}{d}$ increases when $\text{CH}^2$ accumulates in molecules.

Landolt, in his turn, has reopened the question, and we may deduce from his experiments:*

1st. That generally an increase in the number of atoms of carbon and hydrogen produces an increase of the index of refraction, but that sometimes the reverse of this happens. Thus the benzoate of ethyl has an index of refraction lower than that of benzoate of methyl.

2nd. That the specific refractive energy $\frac{n-1}{d}$ increases when the number of $\text{CH}^2$ increases, but that the quantities by which this value augments are unequal, and diminish progressively as $\text{CH}^2$ is added to bodies more and more rich in carbon and hydrogen.

3rd. That the refraction-equivalent $\frac{\text{P}n^2-1}{d}$ increases by a constant quantity, which is about 7·6 for each addition of $\text{CH}^2$.

Instead of experimenting on bodies classed in homologous series, we may operate upon bodies grouped in series according to characters other than the addition of $n\text{CH}^2$. Thus there are bodies whose empirical formulæ present constant differences between each other, but which have different functions. The study of such bodies enables us to determine, with more or less precision, the influence which their chemical constitution exercises on light. It is found that bodies which present the same difference in their composition do not give equal differences in the value $\frac{n-1}{d}$ P, as in cases in which their chemical constitution is the same. The causes which determine the agreement or differences in these numbers become very clear when the rational formulæ are examined. It is seen that the grouping does not exercise any influence on the value of the specific refractive energy when the bodies under consideration are derived from the same type, but that, on the contrary, it exercises considerable influence when these bodies belong to different types. Thus the refraction-equivalents of acetone $\left(\begin{matrix}C^2H^3O \\ CH^3\end{matrix}\right\}\Big)$ and propylic aldehyd $\left(\begin{matrix}C^3H^5O \\ H\end{matrix}\right\}\Big)$ differ about equally from that of butyric acid, because propylic aldehyd and ordinary acetone are very similarly constituted.

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* See Poggendorf's *Annalen*, cxxiii. 608 and 609, table iv.

The other series besides the homologous, studied by Landolt, are those of bodies whose formulæ differ by $nC$, by $nH^2$, and by $nO$; omitting certain very refractive bodies which do not follow the same laws exactly.

In those bodies which differ by $nC$, it is observed that the density and index of refraction diminish as the number of C increases, that the specific refractive energy $\frac{n-1}{d}$ does not obey any regular and simple law, but that the refraction-equivalent $\frac{Pn-1}{d}$ increases about equally for each C added.

For bodies differing by $nH^2$, the density, index of refraction, and specific refractive energy $\frac{n-1}{d}$, constantly increase with the augmentation of the number of $H^2$, and it is the same with the refraction-equivalent $\frac{Pn-1}{d}$.

Each addition of O causes an elevation of the density and index of refraction, a diminution of the value $\frac{n-1}{d}$, and a tolerably regular increase of the value $\frac{Pn-1}{d}$.

Useful results are furnished by the modification of the refraction-equivalent $\frac{Pn-1}{d}$, which, by the addition of each element, increases by a determined quantity partly depending on the constitution of the substance. It has been seen that two groups of bodies, which differ among themselves by equal numbers of atoms of the same nature, present differences in their refraction-equivalents, which differences are almost equal when the bodies are derived from the same type. Thus for each addition of C, the difference is from 5·41 to 5·43, when the two bodies compared are monatomic, and are derived, one from the water type $\left.\begin{matrix}H\\H\end{matrix}\right\}O$, and the other from the hydrogen type $\left.\begin{matrix}H\\H\end{matrix}\right\}$, as is the case with methylic alcohol $\left(\left.\begin{matrix}CH^3\\H\end{matrix}\right\}O\right)$ and the hydride of acetyl $\left(\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}\right)$; ethylic alcohol $\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)$ and acetone $\left(\left.\begin{matrix}C^2H^3O\\CH^3\end{matrix}\right\}\right)$.

The differences change and vary between 4·75 and 4·80 when the compounds are, one monatomic and the other biatomic. As, for instance, lactic acid $\left(\left.\begin{matrix}C^3H^4O''\\H^2\end{matrix}\right\}O^2\right)$ and acetic anhydride $\left(\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O\right)$; glycol $\left(\left.\begin{matrix}C^2H^4\\H^2\end{matrix}\right\}O^2\right)$ and propionic acid $\left(\left.\begin{matrix}C^3H^5O\\H\end{matrix}\right\}O\right)$.

These observations are also applicable to bodies which differ, not by $nC$, but by $nH^2$ or by $nO$. It will be seen that for the same number of $H^2$ or O more or less, the differences between the refraction-equivalents of monatomic bodies are not quite the same as those of the refraction-equivalents of polyatomic bodies; moreover, with bodies having great specific refractive energy, irregularities are observed which are owing to the disturbing influence of dispersion, which influence may be diminished by replacing the index of refraction found $\mu$ by the index deduced from Cauchy's formula $\mu = \frac{A + B}{\lambda^2}$; but its effect is still not entirely removed, Cauchy's formula not being perfectly exact.

## *Indices of the Refraction of the Elements.*

As the refraction-equivalents of bodies whose formulæ differ by $nC$ themselves differ by $n(4{\cdot}75\text{–}5{\cdot}43)$, and as the differences corresponding to the increase of the number of atoms of hydrogen and oxygen are, for $nH^2$, 2·66–2·12, and for $nO$, 3·24–2·45, let the mean be:

| | | |
|---|---|---|
| For each C . . . . . | 5·09 | |
| — $H^2$ . . . . . | 2·40 | thence for each H — 1·20 |
| — O . . . . . | 2·85. | |

The numbers 5·09, 1·20, and 2·85, respectively represent the refraction-equivalent of carbon, hydrogen, and oxygen.

These numbers may be arrived at in another way:

It has been seen that the addition of $nCH^2$ raises the refraction-equivalent $n7{\cdot}60$. If from the refraction-equivalent of the acids $C^nH^{2n}O^2$, which may be represented by the formula $C^nH^{2n}+O^2$, the value corresponding to $nCH^2$ be subtracted, there remains for $O^2$ the (mean) number 6, that is to say for O, the number 3.

If, on the other hand, from the refraction-equivalent of the alcohols $C^nH^{2n+2}O$, the values corresponding to $nCH^2$ and to O be subtracted, there remains 2·6 for the value of $H^2$ or 1·30 for that of H.

The refraction-equivalent of $CH^2$, deduced from the observation of homologous series, being 7·60, on deducting that of $H^2$—say 2·60—we have that of carbon = 5. Landolt thinks that these latter numbers are the most correct, and he therefore adopts:

For the refraction-equivalent of carbon . . . . 5·00
— — of hydrogen . . . 1·30
— — of oxygen . . . . 3·00

It would be interesting to know whether the refraction-equivalents of the same bodies in the free state would be the same as the preceding. The data we possess on this point are unfortunately not to be depended upon; but we know that in the case of the diamond its index of refraction taken in relation to the red ray = 2·434 . . . and its density = 3·55. The atomic weight of carbon being 12, we get from these numbers:

$$\frac{Pn-1}{d} = \frac{12 \times 2{\cdot}434 - 1}{3{\cdot}55} = 4{\cdot}85.$$

For hydrogen, the index of refraction in relation to the red ray is 1·000138, according to Dulong; and the density, according to Regnault, = 0·06927, thus P = 1. We have therefore:

$$\frac{Pn-1}{d} = \frac{1 \times 1{\cdot}000138}{0{\cdot}6927} = 1{\cdot}54.$$

For oxygen, the index equals 1·000272, the density 1·10561, and the atomic weight 16, thence:

$$\frac{Pn-1}{d} = \frac{16 \times 1{\cdot}000272}{1{\cdot}10561} = 3{\cdot}04.$$

These numbers approaching so closely those deduced from the study of organic compounds, it is very probable that the refraction-equivalent of these elements remains the same, whether they be in the free state or in combination.

### *Calculation of the Indices of Refraction of Bodies corresponding to the Formula* $C^nH^mO^x$ *from the Indices of their Constituent Elements.*

Grailich, Waifs, Hoek, Schrauff, and others, have given formulæ which enable us to calculate the index of refraction of a mixture of liquids, when the centesimal composition in volume and the density of this mixture are known, along with the index of refraction of each of the liquids of which the mixture is composed. Biot and Arago have also given the following formula for calculating the index of refraction of mixed gases:

$$\frac{N^2-1}{D} P = \frac{n^2-1}{d} p + \frac{n^2_{\prime}-1}{d_1} p_{\prime} \ldots\ldots + \frac{n^2_{\prime\prime}-1}{d_{\prime\prime}} p_{\prime\prime}$$

in which N is the index of refraction of the mixture, D its density, P its molecular weight, that is to say, the mean of the molecular weights of its components; and $n$ $d$ $p$ the corresponding values of each of these components.

When applied to liquids, this formula becomes:

$$\frac{N-1}{D} P = \frac{n-1}{d} p + \frac{n_1-1}{d_1} p_1 \cdot \cdot \cdot \cdot \cdot \cdot + \frac{n_n-1}{d_n} p_n.$$

Landolt has calculated the indices of refraction of several mixtures according to the equation: $N = \dfrac{1+\dfrac{n-1}{d}p+\dfrac{n_1-1}{d_1}p_1}{p+p_1}$. N has been taken relatively to the line $\alpha$ of the hydrogen spectrum. The results have always closely approximated to those furnished by experiment, as will be seen from the following table:

| Names of Bodies. | Found. | | | Calculated |
|---|---|---|---|---|
| | $p$ | $d$ | $\mu\alpha$ | $\mu\alpha$ |
| 3 methyl-alcohol . . . | 96 | 0·7964 | 1·3279 | |
| 1 methyl-alcohol . . . | 88 | 0·8135 | 1·4057 | |
| Mixture . . . . . . . | 184 | 0·8038 | 1·3640 | 1·3644 |
| 2 ethyl-alcohol . . . . | 92 | 0·8011 | 1·3605 | |
| 1 amyl-alcohol . . . . | 88 | 0·8135 | 1·4057 | |
| Mixture . . . . . . . | 180 | 0·8065 | 1·3822 | 1·3821 |
| 1 ethyl-alcohol . . . . | 46 | 0·8011 | 1·3605 | |
| 2 amyl-alcohol . . . . | 176 | 0·8135 | 1·4057 | |
| Mixture . . . . . . . | 222 | 0·8104 | 1·3961 | 1·3960 |
| 1 acetic acid. . . . . | 60 | 1·0518 | 1·3706 | |
| 1 butyric acid . . . . | 88 | 0·9610 | 4·3953 | |
| Mixture . . . . . . . | 148 | 0·9930 | 1·3850 | 1·3847 |
| 1 ethyl-alcohol . . . . | 46 | 0·8011 | 1·3605 | |
| 1 formic acid . . . . | 46 | 1·2211 | 1·3693 | |
| Mixture . . . . . . . | 92 | 0·9602 | 1·3610 | 1·3612 |
| 1 benzoic aldehyd . . . | 106 | 1·0474 | 1·5391 | |
| 1 formic acid . . . . | 46 | 1·2211 | 1·3693 | |
| Mixture . . . . . . . | 152 | 1·0876 | 1·4900 | 1·4900 |

These rules which are applicable to the calculation of the index of refraction of mixtures may also be applied to that of compounds, as M. Landolt demonstrates. The value $\frac{\mu-1}{d}$ of a liquid $C^nH^mO^x$ entirely depends on the empirical formula, and not at all or very little on the rational formula.

The equation then becomes:

$$\frac{N-1}{D}P = \frac{n-1}{d}gm + \frac{n_1-1}{d_1}g_1m_1 + \frac{n_2-1}{d_2}g_2m_2 + \ldots\ldots\ldots$$

or

$$P = gm + g_1m_1 + g_2m_2 \ldots\ldots$$

etc., the product $\frac{n-1}{d}$ by the atomic weight may be written:

$$\frac{N-1}{D}P = R\,;\ \frac{n-1}{d}g = r\,;\ \frac{n_1-1}{d_1}g_1 = r_1 \ldots\ldots$$

etc.

When the values of $r$, $r_1$, $r_2$, that is to say, the refraction-equivalents of the elements are known, we may thence deduce the value R of a compound containing $m$ atoms of the first element, $m_1$ atoms of a second, and $m_2$ atoms of a third. Thus we have $R = mr + m_1r_1 + m_2r_2$; which is the same as to say that the refraction-equivalent of the mixture $\frac{N-1}{D}P$ is equal to the sum of the refraction-equivalents of the constituent atoms; and that it may be calculated absolutely in the same manner as the molecular weight.

The refraction-equivalents calculated with the index $\mu a$ being known for C, H, and O, and being equal to 5 for C, 1·3 for H, and 3 for O, the refraction-equivalents of the liquids $C^nH^mO^r$ may be easily calculated. Thus for alcohol $C^2H^6O$ we have: the refraction-equivalent of $C^2H^6O = 2(5{\cdot}00) + 6(1{\cdot}30) + 1(3{\cdot}00) = 20{\cdot}80$, from which N may be deduced according to the equation $N = 1 + \frac{R}{P+D}$.

This calculation is very simple, and serves to determine with sufficient accuracy the index of refraction of many organic liquids, both mono- and poly-atomic; but it is not applicable to bodies whose refractive power is very great.

### *Optical Analysis.*

Landolt has found that by means of the specific refractive energy $\frac{\mu a - 1}{d}$, the centesimal composition of a liquid composed of two or even three elements may be determined.

He first remarked that the value $\frac{n-1}{d}$ remains constant when the temperature augments or diminishes, $n$ being diminished at the same time as $d$.

He also established that the relation between the specific refractive energy of a mixture and that of its components may be expressed by the formula $\frac{N-1}{D}P = \frac{n-1}{d}p + \frac{n'-1}{d'}p'$, in which $p$ and $p'$ indicate the weight of the components expressed in parts of P the weight of the mixture; if therefore the value $\frac{N-1}{D}$ of a mixture be determined at any temperature, and if $\frac{n-1}{d}$ and $\frac{n'-1}{d'}$ be known, it is easy, when the mixture only contains two liquids, to determine the proportion in hundredth parts, making $P = 100$. We have the three following equations:

1st. $$\frac{100N-1}{D} = \frac{n-1}{d}p + \frac{n'-1}{d'}(100-p)$$

2nd. $$p = \frac{100\left(\frac{N-1}{D} - \frac{n'-1}{d'}\right)}{\frac{n-1}{d} - \frac{n'-1}{d'}}$$

3rd. $$p' = 100 - p.$$

In order to verify this method, Landolt made the following observations. The indices of refraction having been determined at 20° in relation to the red line of the hydrogen spectrum—

A first mixture was made containing : ordinary alcohol . . 51·1
amylic alcohol . . . 48·9

and a second mixture which contained : ethylic alcohol . . . 20·7
and amylic alcohol . 79·3

For amylic alcohol $n = 1\cdot4057$, $d = 0\cdot8135$ and $\frac{n-1}{d} = 0\cdot4987$.

For ordinary alcohol $n = 1\cdot3606$, $d = 0\cdot8011$ and $\frac{n_1-1}{d_1} = 0\cdot4501$.

In the first mixture N would equal 1·3822, $D = 0\cdot8065$ and $\frac{N-1}{D} = 0\cdot4738$.

In the second mixture N would equal 1·3961, $D = 0\cdot8104$ and $\frac{N-1}{D} = 0\cdot4887$.

These numbers give the quantity of amylic alcohol contained in the two mixtures, according to the equations:

$$p = \frac{47\cdot38 - 45\cdot01}{0\cdot4987 - 0\cdot4501} = 48\cdot8$$

$$\frac{48\cdot87 - 41\cdot01}{0\cdot4987 - 0\cdot4501} = 79\cdot3$$

If these numbers were subtracted from 100 to obtain the proportion of ethylic-alcohol, we have, lastly:

| | 1st mixture. | | 2nd mixture. | |
|---|---|---|---|---|
| | Calculated composition. | True composition. | Calculated composition. | True composition. |
| Amyl-alcohol . . | 48·8 | 48·9 | 79·4 | 79·3 |
| Ethyl-alcohol . . | 51·2 | 51·1 | 20·6 | 20·7 |

This analytical method is excellent whenever a mixture only contains two liquids, and may even be extended to cases where it contains three; but the indices of refraction must then be taken in relation to several lines, when errors in observation are apt to occur, and the results of the analysis cannot be relied on.

Though limited, the method of optical analysis just described may be of much service. Great care must be taken when it is employed to determine the index of refraction and the density at the same temperature of one liquid. But the indices of refraction and the densities of different liquids may be taken at different temperatures, as the value $\frac{n-1}{d}$ remains constant.

Landolt has made a series of experiments to ascertain what is the influence exercised by errors of observation on the results of the analysis. He determined $n$ and $d$ at three different times and at different temperatures for a mixture of chloroform and alcohol, and for each of these liquids separately. He thus obtained for the refraction-equivalents of these three liquids numbers which differed indeed, but were nearly the same. By combining these numbers he was able to form 27 equations. The quantity of alcohol found by the mean result of these 27 equations was 13·02, the real quantity being 13·11; the greatest deviation for alcohol was 0·26, and the greatest difference between the different analyses 0·32.

This analytical method gives results which are the more certain the more the specific refractive energies $\frac{n-1}{d}$ of the two liquids mixed differ, and are usually so exact that the variations only affect the first decimal, and are not greater than those which attend the best analytical methods.

Optical analysis has been applied to the study of the products of a fractional distillation. A mixture of 200 grammes of ordinary alcohol and 200 grammes of amylic alcohol was divided into 7 parts, passing over below 130° or 132°; the indices of refraction and the densities of the pure liquids were:

| | $n$ | $d$ | $\frac{n-1}{d}$ |
|---|---|---|---|
| Of ethylic alcohol . . | 1·3620 | 0·7975 | 0·4539 |
| amylic alcohol . . | 1·4076 | 0·8099 | 0·5033 |

The products of the distillation furnished the following results: the weights of the portions distilled are expressed in hundredth parts of the entire quantity:

| Portion . . . | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Boiling point . | 80°-90° | 90°-100° | 100°-110° | 110°-120° | 120°-130° | 130°-131° | 131°-132° |
| Quantity in hundredth parts of the product collected . . | 23·5 | 22·5 | 12 5 | 7·0 | 9·0 | 5·5 | 18 |
| $n$ . . . . . | 1·3680 | 1·3712 | 1·3781 | 1·3871 | 1·3983 | 1·4054 | 1·4075 |
| $d$ . . . . . | 0·8003 | 0·8020 | 0·7995 | 0·8109 | 0·8060 | 0·8091 | 0·8094 |
| $\frac{n-1}{d}$ . . . | 0·4598 | 0·4628 | 0·4729 | 0·4774 | 0·4942 | 0·5011 | 0·5032 |
| Ethyl-alcohol . | 88·1 | 82·0 | 61·5 | 52·4 | 18·4 | 4·5 | 0·2 |
| Amyl-alcohol . | 11·9 | 18·0 | 38·5 | 47·6 | 81·6 | 95·5 | 99·8 |
| | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 |

This example shows what assistance may be rendered by optical analysis in the study of fractional distillations; it can also be used to determine in what quantities two liquids are mixed. Thus on shaking water and ether together, and then separating the two layers, it will be found that the upper layer contains 95·19 parts of ether and 4·1 of water, while the lower layer contains 8·2 of ether and 91·8 of water.

Optical analysis may also be used in the study of diffusion; might it not also be employed to study the solutions of solids in liquids? Dr. Gladstone's works in relation to the refracting power $\frac{n-1}{d}$ of rock salt, solid and in solution, permit us to hope that eventually this may be the case.

### *Optical Analysis of Compounds.*

The formula used to analyze mixtures is also applicable to compounds, and should give more correct results, since the specific refractive energies of their elements are known. As most of the organic compounds are ternary, it is necessary to determine the indices of refraction relatively to three lines: red $\alpha$, green $\beta$, and violet $\gamma$ of hydrogen. The following are the values of C, H, and O:

| | $\frac{n\alpha-1}{d}$ | $\frac{n\beta-1}{d}$ | $\frac{n\gamma-1}{d}$ |
|---|---|---|---|
| C . . . . | 0·42205 | 0·43093 | 0·43738 |
| H . . . . | 0·30160 | 1 31610 | 1·31930 |
| O . . . . | 0·17280 | 0·17596 | 0·17703 |

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By means of these and of the indices of refraction $N\alpha$, $N\beta$, and $N\gamma$ of a body composed of hydrogen, carbon, and oxygen, whose density D is supposed to be known, the centesimal composition of the body may be calculated. In order to understand the principle of this calculation, let us first place: $100\frac{N\alpha-1}{D}=A$; $100\frac{N\beta-1}{D}=B$; $100\frac{N\gamma-1}{D}=C$: let us call the centesimal proportion of the carbon $x$, that of the hydrogen $y$, and that of the oxygen $z$. We shall have:

$$\begin{aligned} 0{\cdot}42205\,x + 1{\cdot}30160\,y + 0{\cdot}17280\,z &= A \\ 0{\cdot}43093\,x + 1{\cdot}31610\,y + 0{\cdot}17596\,z &= B \\ 0{\cdot}43738\,x + 1{\cdot}31930\,y + 0{\cdot}17703\,z &= C \end{aligned}$$

from which equation we may ascertain the three unknown values.

The following examples show how far this analytical method is correct:

*Ethyl-alcohol* $C^2H^6O$.—$d=0{\cdot}8011$, $n\alpha=1{\cdot}36054$, $n\beta=1{\cdot}36665$ and $n\gamma=1{\cdot}36997$; from which: $A=45{\cdot}005$; $B=45{\cdot}768$; $C=46{\cdot}183$: deducing the centesimal composition of alcohol from these numbers they give as the

| | Composition found. | The true composition being |
|---|---|---|
| C . . . . | 51·9 | 52·2 |
| H . . . . | 12·9 | 13·0 |
| O . . . . | 36·2 | 34·8 |
| | 101·0 | 100·0 |

*Amyl-alcohol.*—$d=0{\cdot}8135$; $n\alpha=1{\cdot}40573$; $n\beta=1{\cdot}41278$; $n\gamma=1{\cdot}41689$: thence, $A=49{\cdot}874$; $B=50{\cdot}741$; $C=51{\cdot}246$: from which for the centesimal composition we get—

| | Composition found. | The true composition being |
|---|---|---|
| C . . . . | 68·0 | 68·2 |
| H . . . . | 13·3 | 13·6 |
| O . . . . | 21·9 | 18·2 |
| | 103·2 | 100·0 |

As will be seen, the figures referring to carbon and hydrogen are sufficiently exact. The difference is only great in the case of oxygen, and this is because the specific refractive energy of this element is not well known.

The formula $\frac{N-1}{D}P=\frac{n-1}{d}p+\frac{n_1-1}{d_1}p_1\ldots$ can only be used for bodies of slight refractive power.

If only binary compounds were to be analyzed, this might be done by knowing the index of refraction relatively to a single ray for the compound and for each of its elements: in the case of water $H^2O$, the specific refractive energy of oxygen $\frac{n-1}{d}$ not being well known, only approximate results can be obtained: the following is the equation which gives these results:

$$1{\cdot}30160x + 0{\cdot}17280(100-x) = 33{\cdot}111$$

in which $x$ is the quantity of hydrogen. This gives $x = 14$ per 100 instead of 11·11, which is its correct value.

Figures more nearly approaching the truth are found with the liquid hydrocarbides.

Thus, for amylene, we have: $D = 0{\cdot}6733$; $N\alpha = 1{\cdot}37061$; and $\frac{N\alpha - 1}{D} = 0{\cdot}55044$. Determining H by the equation:

$$1{\cdot}30160x + 0{\cdot}42205(100-x) = 55{\cdot}044$$

We find

| | | The true composition being |
|---|---|---|
| C . . . . | 85·4 | 85·7 |
| H . . . . | 14·6 | 14·3 |

In applying optical analysis to compounds, the results are more correct the better the specific refractive energies of their elements are known. These energies being as yet only approximately known, it is evident that this analytical method is at present only theoretical. But besides the possibility of its eventually becoming applicable, its theoretical possibility shows relations of considerable importance between the specific refractive energies and the composition of bodies.

## HISTORY OF SYNTHESIS IN ORGANIC CHEMISTRY.

In chemistry, analysis has long been distinguished from synthesis. By the former, a given body is separated into its elements; by synthesis, on the contrary, the elements being given, the body is reconstituted.

Previous to the last twenty-five years, organic chemistry only possessed the first of these methods of investigation. Bodies were decomposed by degrees, by submitting them to the action of different agents, and starting from a complex compound, its elements were thus arrived at, passing through several more simple intermediate compounds. By means of these new compounds or of the elements, the original body was never built up again. In other words, synthesis did not exist.

During the last quarter of a century, organic chemistry has become possessed of this synthetical method so much wanted. In this chapter we intend to give an account of the different methods used for the realization of this important object. But first it will be well to define the meaning to be attached to the word synthesis.

As we have just said, synthesis is the opposite of analysis. By the latter, a compound is reduced to its elements, or at least transformed into other more simple compounds; by synthesis, compound bodies are formed directly from their elements, or, at least, from compounds less complex than themselves. Briefly, in analysis, the molecular complication is diminished, in synthesis it is increased.

However, if such an extensive acceptation were given to the word synthesis, an entire volume, instead of a chapter, would here be required; we must therefore use the term in a more limited sense.

In fact, if we consider the different reactions which increase the molecular complication of bodies, we shall see that very different cases occur, as the following examples show.

If alcohol be submitted to the action of sulphuric acid, ether is obtained; now the formula of alcohol is $C^2H^6O$, and that of ether $C^4H^{10}O$.

So if acetic acid acts on ethylamine, acetate of ethylamine, the empirical formula of which is $C^4H^{11}NO^2$, is obtained, while the formula of acetic acid is $C^2H^4O^2$, and that of ethylamine $C^2H^7N$.

In the production of acetate of ethylamine, as in that of ether, a compound is formed the molecule of which is more complicated than that of its generators; in other words, a synthesis is accomplished, if the wider acceptation mentioned above be attributed to this word.

However, if the new bodies formed be submitted to active reagents, and the products which arise are examined, it is observed that these products are the same as are produced when, not the compounds obtained synthetically, but their generators, are submitted to the same reactions.

For instance, the action of acetic acid on alcohol gives acetate of ethyl and water, and it is still acetate of ethyl and water which are formed when acetic acid is submitted to the action of ether:

$$\underset{\text{Alcohol.}}{(C^2H^6O)} + \underset{\text{Acetic acid.}}{(C^2H^4O^2)} = \underset{\text{Acetic ether.}}{(C^4H^8O^2)} + \underset{\text{Water.}}{(H^2O)}$$

$$\underset{\text{Ether.}}{(C^4H^{10}O)} + \underset{\text{Acetic acid.}}{2(C^2H^4O^2)} = \underset{\text{Acetic ether.}}{2(C^4H^8O^2)} + \underset{\text{Water.}}{(H^2O)}$$

Analogous facts are observed with the acetate of ethylamine.

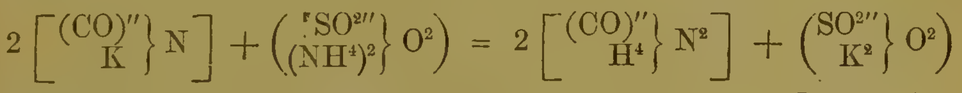
It appears therefore that in ether, as in acetate of ethylamine, the radicles which unite to form a molecule more complicated than the original one, remain in a certain state of mutual independence, and again separate under the influence of suitable reagents.

Let us now suppose that sodium and carbonic anhydride act simultaneously on phenol, the sodic salt of salicylic acid would be obtained, and a synthesis would thus be realized, since, starting from phenol $C^6H^6O$, salicylic acid $C^7H^6O^2$ would be prepared.

This synthesis is very different from the preceding, In fact, though in certain cases, under powerful influences, salicylic acid can split up into phenol and carbonic anhydride, in the greater number of reactions, this acid would give rise to products entirely different from those that could be prepared from carbonic anhydride or phenol: these derivatives would have in reality about the same complication as salicylic acid itself.

It will be seen that there is a great difference between the two kinds of syntheses just mentioned. Though, admitting that the reactions of the first class are to some extent synthetical, we consider that the name of synthesis should be reserved exclusively for the production of a substance more complicated than its generators, and capable of entering integrally into reactions, giving bodies whose molecule is about as complicated as its own. In cases in which a body is obtained from its elements or from another body, itself prepared from the elements, we say it is obtained entirely by synthesis.

We owe one of the earliest cases of organic synthesis to Wœhler. In 1828 this chemist discovered a process by which urea may be prepared by means of its elements. Although urea has not the characters of the cyanates, it possesses the same composition as the cyanate of ammonium. Wœhler has shown that when a solution of sulphate of ammonium is boiled with a solution of cyanate of potassium, and evaporated to dryness, the residue treated with alcohol yields urea, which may be obtained crystallized by the spontaneous evaporation of the alcohol: it is evident that ammonic cyanate is first formed in this case, and is afterwards transformed into its isomer urea:



$$2\left[\left.\begin{matrix}(CO)''\\K\end{matrix}\right\}N\right]+\left(\left.\begin{matrix}SO^{2''}\\(NH^4)^2\end{matrix}\right\}O^2\right)=2\left[\left.\begin{matrix}(CO)''\\H^4\end{matrix}\right\}N^2\right]+\left(\left.\begin{matrix}SO^{2''}\\K^2\end{matrix}\right\}O^2\right)$$

Potassic cyanate. Sulphate of ammonium. Urea. Potassic sulphate.

Since then, about 1845, Kolbe made an experiment which abounded in synthetical results: by causing dry chlorine to act on sulphide of carbon, he succeeded in replacing the sulphur of this compound by chlorine, and thus obtained the tetrachloride of carbon $CCl^4$:

$$CS^2 + 4Cl^2 = CCl^4 + 2(SCl^2)$$

Sulphide of carbon. Chlorine. Tetrachloride of carbon. Chloride of sulphur.

In the course of the same year, the same chemist succeeded in preparing trichloracetic acid by causing chlorine and water to act simultaneously on the protochloride of carbon $C^2Cl^4$. This reaction takes place in two stages; in the first, the protochloride of carbon is converted into sesquichloride, and in the second, this latter body is transformed into hydrochloric and trichloracetic acids:

$$(C^2Cl^4) + \left.\begin{matrix}Cl\\Cl\end{matrix}\right\} = (C^2Cl^6)$$

Protochloride of carbon. Chlorine. Sesquichloride of carbon.

$$\underset{\substack{\text{Sesquichloride}\\\text{of carbon.}}}{(C^2Cl^6)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Trichloracetic acid.}}{\left(\left.\begin{array}{r}C^2Cl^3O\\H\end{array}\right\}O\right)} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{3\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)}$$

As, moreover, the tetrachloride $CCl^4$ gives protochloride $C^2Cl^4$, when its vapours are passed through a red hot tube:

$$\underset{\substack{\text{Tetrachloride}\\\text{of carbon.}}}{2(CCl^4)} = \underset{\text{Chlorine.}}{Cl^4} + \underset{\substack{\text{Protochloride}\\\text{of carbon.}}}{(C^2Cl^4)}$$

the complete synthesis of trichloracetic acid is accomplished.

In 1845, also, M. Melsens discovered that nascent hydrogen, disengaged by means of sodium, possesses the property of being substituted for the chlorine of chlorinated organic substances, and by this reaction, to which he gave the name of inverse substitution, he succeeded in converting trichloracetic into acetic acid:

$$\underset{\text{Trichloracetic acid.}}{\left(\left.\begin{array}{r}C^2Cl^3O\\H\end{array}\right\}O\right)} + \underset{\text{Hydrogen.}}{3\left(\left.\begin{matrix}H\\H\end{matrix}\right\}\right)} = \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{3\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Acetic acid.}}{\left(\left.\begin{array}{r}C^2H^3O\\H\end{array}\right\}O\right)}$$

About the same time, Kolbe, by causing sulphide of carbon to act, not on dry but on moist chlorine, obtained a body since called trichloromethyl-sulphurous chloride, whose formula is $(CCl^4SO^2)$. This body, when submitted to the action of potash, exchanges an atom of chlorine for hydroxyl (OH), and furnishes trichloro-methyl-sulphurous acid $(CCl^3HSO^3)$, which, when decomposed by nascent hydrogen developed by means of galvanism, gives bichloro-methyl-sulphurous acid $(CCl^2H^2SO^3)$, chloro-methyl-sulphurous acid $(CClH^3SO^3)$, and methyl-sulphurous acid $(CH^4SO^3)$.

At the end of 1845, chloride of carbon, acetic acid, and the series of sulphuretted acids just mentioned, had been obtained by synthesis; and, further, having acetic acid, marsh gas could be prepared by distilling acetate of sodium with soda-lime. However, this preparation was very indirect; but in 1846, Melsens accomplished the synthesis of marsh gas by submitting tetrachloride of carbon to inverse substitution:

$$\underset{\substack{\text{Tetrachloride}\\\text{of carbon.}}}{(CCl^4)} + \underset{\text{Hydrogen.}}{4\left(\left.\begin{matrix}H\\H\end{matrix}\right\}\right)} = \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{4\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Marsh gas.}}{(CH^4)}$$

From 1846 to 1850, no progress was made in synthesis; but in a series of experiments commenced in 1850 and terminated in 1851, Frankland succeeded in preparing methyl $\left.\begin{matrix}CH^3\\CH^3\end{matrix}\right\}$ and ethyl $\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}$ by means of the corresponding alcohols. To effect this, he caused zinc to act on the hydriodic ethers of these alcohols. The reaction takes place in two stages; in the first, iodide of zinc is formed, and a compound of this latter metal with ethyl or methyl; in the second, this organo-metallic compound reacts with a second molecule of the hydriodic ether employed, and gives rise to the corresponding hydrocarbide:

$$\text{1st.}\quad \underset{\text{Iodide of methyl}}{2\left(\left.\begin{matrix}CH^{3}\\ I\end{matrix}\right\}\right)} + \underset{\text{Zinc.}}{2Zn''} = \underset{\text{Iodide of zinc.}}{(Zn''I^{2})} + \underset{\text{Zinc-methyl.}}{\left(Zn''\left\{\begin{matrix}CH^{3}\\ CH^{3}\end{matrix}\right.\right)}$$

$$\text{2nd.}\quad \underset{\text{Zinc-methyl.}}{\left(Zn''\left\{\begin{matrix}CH^{3}\\ CH^{3}\end{matrix}\right.\right)} + \underset{\text{Iodide of methyl.}}{2\left(\left.\begin{matrix}CH^{3}\\ I\end{matrix}\right\}\right)} = \underset{\text{Iodide of zinc.}}{(Zn''I^{2})} + \underset{\text{Methyl.}}{2\left(\left.\begin{matrix}CH^{3}\\ CH^{3}\end{matrix}\right\}\right)}$$

At the time of this discovery it was not considered as a synthesis. Formulæ less by half than those by which they are now represented were given to the hydrocarbides, and the radicles $CH^3$ and $C^2H^5$ contained in the iodides of methyl and ethyl were believed to be isolated. It is true that Gerhardt almost immediately showed that it was necessary these formulæ should be doubled; but while doing this, he considered these bodies as analogous to hydrogen, and supposed that their molecules contained two atoms of the same radicle in a certain state of mutual independence. The result was that, by Gerhardt and the other chemists of this period, the fact discovered by Frankland was considered analogous to the formation of compound ethers, and to which we refuse the name of synthesis, according to the limited meaning we attribute to this word. The opinion which was held at the time of Frankland's discovery was retained up to 1864, when Schorlemmer, by causing chlorine to act on free methyl, succeeded in substituting an atom of this metalloid for an atom of hydrogen:

$$\underset{\text{Methyl.}}{(C^{2}H^{6})} + \underset{\text{Chlorine.}}{Cl^{2}} = \underset{\text{Hydrochloric acid.}}{(HCl)} + \underset{\text{Chloride of ethyl.}}{(C^{2}H^{5}Cl)}$$

and thus transforming methyl into chloride of ethyl, from which he prepared ordinary alcohol.

Therefore, starting from methyl prepared by means of wood-spirit $CH^4O$, alcohol $C^2H^6O$ is obtained by a true synthesis.

There are still chemists who believe that methyl and free ethyl contain two independent groups, and that these two groups only unite in an intimate manner under the influence of chlorine. However this may be, as in every synthesis we must look to the commencement and the conclusion, Frankland's reaction is synthetical. For if it were not so itself, it would enable a synthesis to be realized by causing chlorine to act on the product obtained.

Frankland's reaction is especially important on account of its general application. This chemist has in fact obtained, not only methyl and ethyl by means of the process just mentioned, but also the radicles of other alcohols, amyl for instance, and Schorlemmer has shown, on the other hand, that all these radicles can give rise to the same phenomena as methyl.

It will therefore be seen that if, starting from methylic alcohol, we can go up to ethylic alcohol, from the latter ethyl $C^4H^{10}$, and consequently butylic alcohol $C^4H^{10}O$, may be prepared; then, by means of this latter, butyl $C^8H^{18}$, and octylic alcohol $C^8H^{18}O$, etc.

By means of this reaction, we rise therefore in the homologous series, of which however it does not give us all the terms; there would remain the intermediate alcohols $C^3H^8O$, $C^5H^{12}O$, $C^6H^{14}O$, and $C^7H^{16}O$, which could not be obtained synthetically. Fortunately, in 1855, to complete Frankland's discovery, M. Wurtz succeeded in preparing all the series of the analogous hydrocarbides, which renders the synthetical process in question quite general. He called the intermediate hydrocarbides he obtained mixed radicles, and prepared them by causing sodium to act on a mixture of the iodide of one alcohol radicle with that of another. He thus prepared methyl-ethyl $\left.\begin{matrix}CH^3\\C^2H^5\end{matrix}\right\} = C^3H^8$, intermediate between methyl $C^2H^6$ and ethyl $C^4H^{10}$:

$$\underset{\text{Sodium.}}{\left.\begin{matrix}Na\\Na\end{matrix}\right\}} + \underset{\text{Iodide of ethyl.}}{\left(\left.\begin{matrix}C^2H^5\\I\end{matrix}\right\}\right)} + \underset{\text{Iodide of methyl.}}{\left(\left.\begin{matrix}CH^3\\I\end{matrix}\right\}\right)} = \underset{\text{Ethyl-methyl.}}{\left.\begin{matrix}CH^3\\C^2H^5\end{matrix}\right\}} + \underset{\text{Iodide of sodium.}}{2\left(\left.\begin{matrix}Na\\I\end{matrix}\right\}\right)}$$

Having the chloride of methyl, the homologous hydrocarbides $C^2H^6$, $C^3H^8$ . . . . $C^nH^{2n+2}$ may be prepared, and by means of these the corresponding alcohols $C^2H^6O$, $C^3H^8O$ . . . . $C^nH^{2n+2}O$. The synthetical preparation of the chloride of methyl, therefore, renders all the syntheses in question complete.

It has long been known that marsh gas exchanges an atom of hydrogen for chlorine when it is submitted to the action of this metalloid: in these conditions a compound ($CH^3Cl$) is formed identical or isomeric with the chloride of methyl. If it could be shown that those two bodies are identical, or at least that under the influence of powerful reagents they give the same products of decomposition, it would be proved that the series of syntheses just treated of are complete syntheses. M. Berthelot has furnished this proof: in 1855 he succeeded in transforming monochlorinated marsh gas into acetate of methyl, by means of acetate of silver, and he then saponified the acetate thus produced: this is the method afterwards employed by Schorlemmer to transform methyl into alcohol:

$$\underset{\text{Monochlorinated marsh gas.}}{(CH^3Cl)} + \underset{\text{Acetate of silver.}}{\left(\left.\begin{matrix}C^2H^3O\\Ag\end{matrix}\right\}O\right)} = \underset{\text{Chloride of silver.}}{\left.\begin{matrix}Ag\\Cl\end{matrix}\right\}} + \underset{\text{Acetate of methyl.}}{\left(\left.\begin{matrix}C^2H^3O\\CH^3\end{matrix}\right\}O\right)}$$

$$\underset{\text{Acetate of methyl.}}{\left(\left.\begin{matrix}C^2H^3O\\CH^3\end{matrix}\right\}O\right)} + \underset{\text{Potassic hydrate.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic acetate.}}{\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right)} + \underset{\text{Methylic alcohol.}}{\left(\left.\begin{matrix}CH^3\\H\end{matrix}\right\}O\right)}$$

We must here bear in mind that to each alcohol there corresponds an acid derived from it by the substitution of O for $H^2$, and an aldehyd derived by the simple subtraction of $H^2$. Considering that from an alcohol a series of bodies such as simple ethers, compound ethers, ethers proper, etc., may be obtained, we perceive that the process just described furnishes the means of accomplishing the synthesis of a great number of compounds belonging to the series of fatty acids. These are moreover far from being the only ones that may be obtained, the method having recently been extended to the aromatic series.

In the course of 1864 and 1865 MM. Fittig and Tollens obtained synthetically the homologues already known of benzine, toluene $C^7H^8$, xylene $C^8H^{10}$, etc.; they moreover obtained new hydrocarbides of the same series, one of which is an isomer of xylene. The process of these chemists is the same as that by which Wurtz prepared mixed radicles, and consists in causing brominated benzine or toluene to act on the iodide of ethyl, methyl, or of amyl in presence of sodium. The sodium seizes the iodine and bromine, and the two residues unite to form a new hydrocarbide:

$$\underset{\text{Brominated benzine.}}{(C^6H^5Br)} + \underset{\text{Bromide of methyl.}}{(CH^3Br)} + \underset{\text{Sodium.}}{Na^2} = \underset{\text{Bromide of sodium.}}{2(NaBr)} + \underset{\text{Toluene.}}{(C^7H^8)}$$

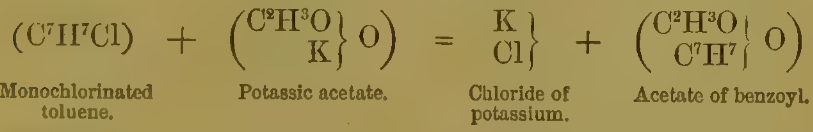
MM. Fittig and Tollens have remarked that it is not a matter of indifference whether bromide of ethyl be made to act on monobrominated benzine or the bromide of methyl on monobrominated toluene; in fact, in the two cases two bodies are formed which are isomeric but not identical.

The hydrocarbides homologous with benzine act the same part in the aromatic series as marsh gas and its homologues perform in the fatty series, and the same methods by which these latter are transformed into corresponding alcohols enable true aromatic alcohols to be prepared from the former.

The experiment has been performed with toluene, which M. Cannizzaro transformed into benzilic alcohol. To effect this, he submitted toluene to the action of chlorine, then boiled the monochlorinated toluene with an alcoholic solution of acetate of potassium, and finally saponified the acetate of benzoyl obtained in this latter reaction:

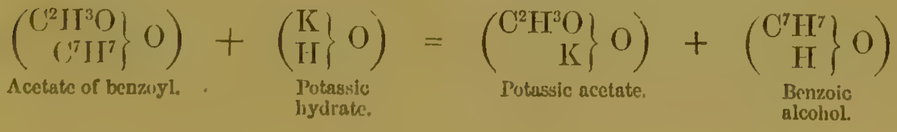
1st. $$\underset{\text{Toluene.}}{(C^7H^8)} + \underset{\text{Chlorine.}}{Cl^2} = \underset{\text{Monochlorinated toluene.}}{(C^7H^7Cl)} + \underset{\text{Hydrochloric acid.}}{(HCl)}$$

2nd.



$$\underset{\text{Monochlorinated toluene.}}{(C^7H^7Cl)} + \underset{\text{Potassic acetate.}}{\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right)} = \underset{\text{Chloride of potassium.}}{\left.\begin{matrix}K\\Cl\end{matrix}\right\}} + \underset{\text{Acetate of benzoyl.}}{\left(\left.\begin{matrix}C^2H^3O\\C^7H^7\end{matrix}\right\}O\right)}$$

3rd.

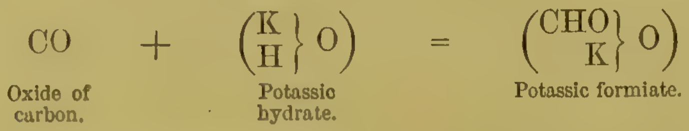


$$\underset{\text{Acetate of benzoyl.}}{\left(\left.\begin{matrix}C^2H^3O\\C^7H^7\end{matrix}\right\}O\right)} + \underset{\text{Potassic hydrate.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic acetate.}}{\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right)} + \underset{\text{Benzoic alcohol.}}{\left(\left.\begin{matrix}C^7H^7\\H\end{matrix}\right\}O\right)}$$

All these are complete real syntheses, they all start from benzine, and in 1858 Berthelot observed that this hydrocarbide is produced, along with naphthalin and several other substances, when a current of the vapour of alcohol is passed through a red-hot porcelain tube. Therefore, as alcohol can be obtained by pure synthesis, so also, we may consider, can benzine and its derivatives.

In 1858 Berthelot succeeded in preparing synthetically marsh gas and some other more complicated carbides of hydrogen. His process is less elegant than those since discovered; but, except in the case of marsh gas which had been already prepared by means of the chloride of carbon, it had the merit of novelty. Berthelot accomplished these syntheses by three different methods.

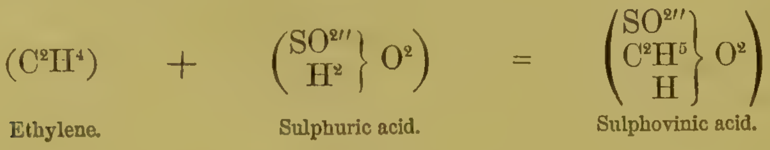
1st. He heated flasks containing oxide of carbon and caustic potash for several days to 100°; the two bodies combined, forming potassic formiate, from which formic acid was extracted:



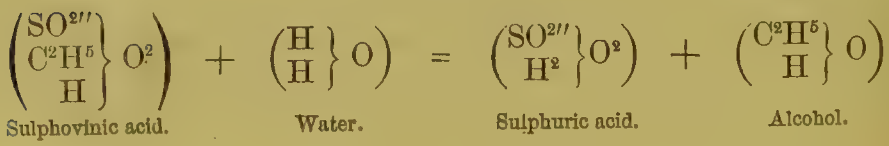
$$\underset{\text{Oxide of carbon.}}{CO} + \underset{\text{Potassic hydrate.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic formiate.}}{\left(\left.\begin{matrix}CHO\\K\end{matrix}\right\}O\right)}$$

Formic acid in vapour, passed through a red-hot tube, gives rise to a very complicated reaction in which marsh gas and ethylene are formed, which are thus prepared synthetically.

By causing ethylene to act on sulphuric acid, the apparatus being well shaken, M. Berthelot succeeded in combining these two bodies, directly, and thus produced sulphovinic acid. When this latter is distilled with water it furnishes alcohol:



$$\underset{\text{Ethylene.}}{(C^2H^4)} + \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)} = \underset{\text{Sulphovinic acid.}}{\left(\left.\begin{matrix}SO^{2''}\\C^2H^5\\H\end{matrix}\right\}O^2\right)}$$



$$\underset{\text{Sulphovinic acid.}}{\left(\left.\begin{matrix}SO^{2''}\\C^2H^5\\H\end{matrix}\right\}O^2\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Sulphuric acid.}}{\left(\left.\begin{matrix}SO^{2''}\\H^2\end{matrix}\right\}O^2\right)} + \underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)}$$

This alcohol, being identical with ordinary alcohol, may be transformed into acetic acid without difficulty. M. Berthelot observed that on passing through a red-hot tube, acetic acid is transformed into a great number of hydrocarbides, among which are found marsh gas $CH^4$, ethylene $C^2H^4$, propylene $C^3H^6$, butylene $C^4H^8$, and amylene $C^5H^{10}$; all therefore obtained by pure synthesis.

2nd. When a mixture of sulphuretted hydrogen and sulphide of carbon in vapour is transmitted over red-hot copper, this latter seizes the sulphur, while the hydrogen and carbon meeting in the nascent state, enter into combination, and give rise to the formation of the hydrocarbides already obtained by the preceding process.

3rd. M. Berthelot has also succeeded in causing the hydrocarbides of the series of ethylene to pass into those of the series of marsh-gas. To effect this, he combines ethylene or its homologues with bromine, which is easily done, and he then heats the bromide to 200° in a sealed tube, with water and potassic iodide. Under these conditions the bromide is decomposed, and while one part of the original hydrocarbide is re-formed, another combines with two atoms of hydrogen arising from a more complete decomposition of a third portion of the mass, and furnishes the hydrocarbides sought for:

$$\underset{\text{Ethylene.}}{(C^2H^{4''})} + \underset{\text{Hydrogen.}}{H^2} = \underset{\substack{\text{Hydride}\\ \text{of ethyl.}}}{(C^2H^6)}$$

$$\underset{\text{Amylene.}}{(C^5H^{10''})} + \underset{\text{Hydrogen.}}{H^2} = \underset{\substack{\text{Hydride}\\ \text{of amyl.}}}{(C^5H^{12})}$$

4th. Lastly, M. Berthelot has observed that, under the influence of a powerful electric current, pure carbon combines with hydrogen and furnishes acetylene $C^2H^2$, which gas gives, with ammoniacal protochloride of copper, a precipitate from which it may afterwards be isolated in a pure state by means of hydrochloric acid. If, instead of hydrochloric acid, nascent hydrogen disengaged by the action of zinc on ammonia at 40° be caused to act on the precipitate, the acetylene unites with two atoms of hydrogen, and ethylene is thus obtained, which in its turn, as we have just said, can be transformed into hydride of ethyl:

$$\underset{\text{Acetylene.}}{(C^2H^2)} + \underset{\text{Hydrogen.}}{H^2} = \underset{\text{Ethylene.}}{(C^2H^4)}$$

M. Berthelot, having obtained methylic alcohol by means of marsh gas, and having prepared the homologues of ethylene as far as amylene, had therefore realized the synthesis of the corresponding alcohols. But as ethylene and its homologues cannot be transformed into saturated hydrocarbides without a great loss of the product, M. Berthelot wished to transform these hydrocarbides directly into alcohols without passing through the corresponding saturated terms. He succeeded perfectly with ethylene and propylene, employing sulphuric acid as before mentioned; but this process was not so successful in the cases of butylene and amylene. M. Berthelot therefore operated in a different manner; he heated the hydrocarbide he wished to transform into alcohol with concentrated hydrobromic or hydrochloric acid, whereby a hydrobromic ether was formed, from which the corresponding alcohol could be readily obtained by submitting this ether to the action of acetate of silver, and saponifying by potash the acetic ether resulting from this latter reaction:

$$\text{1st.}\quad \underset{\text{Ethylene.}}{(C^2H^{4\prime\prime})} + \underset{\text{Hydriodic acid.}}{\left.\begin{matrix}H\\I\end{matrix}\right\}} = \underset{\text{Iodide of ethyl.}}{(C^2H^5I)}$$

$$\text{2nd.}\quad \underset{\text{Iodide of ethyl.}}{(C^2H^5I)} + \underset{\text{Acetate of silver.}}{\left(\left.\begin{matrix}C^2H^3O\\Ag\end{matrix}\right\}O\right)} = \underset{\text{Iodide of silver.}}{\left.\begin{matrix}Ag\\I\end{matrix}\right\}} + \underset{\text{Acetate of ethyl.}}{\left(\left.\begin{matrix}C^2H^3O\\C^2H^5\end{matrix}\right\}O\right)}$$

$$\text{3rd.}\quad \underset{\text{Acetate of ethyl.}}{\left(\left.\begin{matrix}C^2H^3O\\C^2H^5\end{matrix}\right\}O\right)} + \underset{\text{Potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic acetate.}}{\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right)} + \underset{\text{Alcohol.}}{\left(\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O\right)}$$

After having verified, in the case of ethylene, the identity of the alcohol obtained by this process with that obtained by fermentation, and having also proved that butylene and amylene unite with hydriodic acid, just as ethylene and propylene do, M. Berthelot, from analogy, thought that butylic and amylic alcohols prepared by his method would be identical with those of fermentation, but he did not verify this. M. Wurtz, however, in 1862 showed that amylic alcohol prepared by Berthelot's method is simply an isomer of ordinary amylic alcohol, for which reason Wurtz calls the first of these bodies amylic pseudo-alcohol.

So far, in all the syntheses mentioned, the starting-point has always been the formation of hydrocarbides, by means of which alcohols, aldehyds, acids, ethers, compound ammonias, etc., are then obtained.

But we can, nevertheless, ascend a homologous series in an inverse manner. For instance, we can pass from a term of one series to the acid of a higher series. Then, by means of this acid, we can prepare the homologue of the body from which we started, and then take this new body as starting-point in order to obtain a third series, homologous with the two others, and so on.

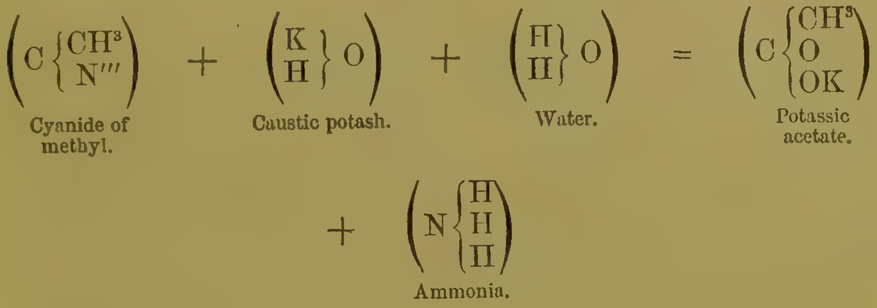
The compounds with which we usually commence are the alcohols. Taking methylic alcohol, for instance, acetic acid, the acid of the next higher series, must be prepared; we then pass from acetic acid to ethylic alcohol, the homologue of methylic alcohol; and in the third place from ethylic alcohol, by means of propionic acid, to propylic alcohol, and so on.

The experiments of M. Pelouze had long shown that, under the influence of hydrating agents, hydrocyanic acid absorbs two molecules of water, and is converted into formiate of ammonium, or, rather, into the products of the decomposition of this salt by the reagents employed. Thus, when potash is used, potassic formiate and ammonia are formed:

$$\underset{\text{Hydrocyanic acid.}}{(CNH)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Ammonic formiate.}}{\left(\left.\begin{matrix}CHO\\(NH^4)\end{matrix}\right\}O\right)}$$

Later, in 1847, MM. Dumas, Malaguti, and Leblanc discovered that a reaction identical with the preceding is produced when the hydrocyanic ethers of the series $(C^nH^{2n+1})CN$ are substituted for hydrocyanic acid. These ethers, under the influence of alkalies, unite with the elements of water, and furnish ammonia, together with the alkaline salt of an acid of the series $C^nH^{2n}O^2$. Thus, commencing with the cyanide of methyl, acetic acid is obtained, and, with the cyanide of ethyl, propionic acid is prepared:

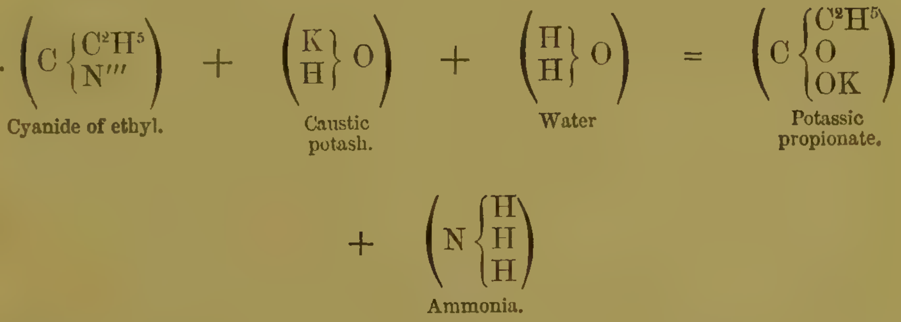
1st.



$$\underset{\text{Cyanide of methyl.}}{\left(C\left\{\begin{matrix}CH^3\\N'''\end{matrix}\right.\right)} + \underset{\text{Caustic potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic acetate.}}{\left(C\left\{\begin{matrix}CH^3\\O\\OK\end{matrix}\right.\right)}$$

$$+ \underset{\text{Ammonia.}}{\left(N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.\right)}$$

2nd.



$$\underset{\text{Cyanide of ethyl.}}{\left(C\left\{\begin{matrix}C^2H^5\\N'''\end{matrix}\right.\right)} + \underset{\text{Caustic potash.}}{\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} + \underset{\text{Water}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Potassic propionate.}}{\left(C\left\{\begin{matrix}C^2H^5\\O\\OK\end{matrix}\right.\right)}$$

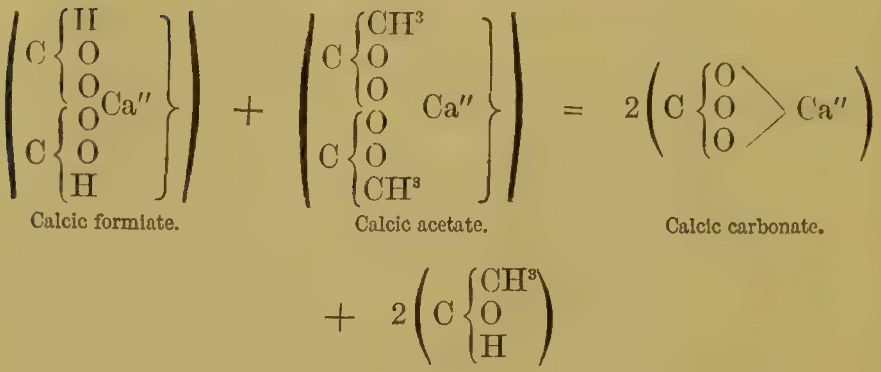
$$+ \underset{\text{Ammonia.}}{\left(N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.\right)}$$

In order to complete the process, it was only necessary to cause the acids to pass into the corresponding alcohols, and this has been done by first transforming the acids into corresponding aldehyds by subtracting an atom of oxygen, and then fixing two atoms of hydrogen on these aldehyds, thereby transforming them into alcohols.

In 1856 Piria and Limpricht separately discovered an identical process for the transformation of monatomic acids into their corresponding aldehyds, which succeeds equally well in all the different series.

In the course of the same year Kolbe gave a different method of arriving at the same result, but as yet this has only been applied in the aromatic series.

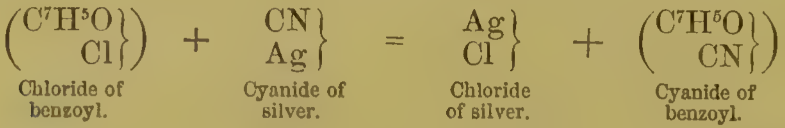
Limpricht and Piria's process consists in distilling an intimate mixture of the calcic salt of the acid whose aldehyd is to be obtained with formiate of calcium. The carbon and oxygen of the formiate are disengaged in the state of carbonic anhydride, which seizes the calcium contained in the formiate and in the other salt. At the same time an atom of oxygen of this latter salt is also eliminated in the state of carbonate of calcium, while the hydrogen set free by the decomposition of the formiate, unites with the residue of the deoxygenized salt and transforms it into aldehyd:



$$\left(\left.\begin{matrix}C\left\{\begin{matrix}H\\O\\O\end{matrix}\right.\\C\left\{\begin{matrix}O\\O\\H\end{matrix}\right.\end{matrix}\right\}Ca''\right)+\left(\left.\begin{matrix}C\left\{\begin{matrix}CH^3\\O\\O\end{matrix}\right.\\C\left\{\begin{matrix}O\\O\\CH^3\end{matrix}\right.\end{matrix}\right\}Ca''\right)=2\left(C\left\{\begin{matrix}O\\O\\O\end{matrix}\right.>Ca''\right)+2\left(C\left\{\begin{matrix}CH^3\\O\\H\end{matrix}\right.\right)$$

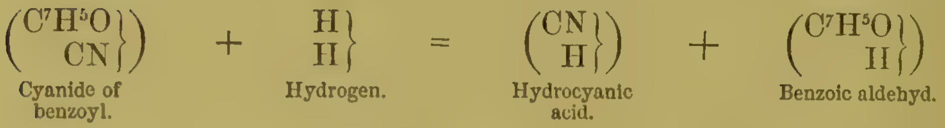
Calcic formiate. Calcic acetate. Calcic carbonate. Aldehyd.

Kolbe's process consists in causing nascent hydrogen to act on the cyanide of an acid radicle, which is itself prepared by heating the chloride of this radicle with cyanide of silver or of mercury:



$$\left(\left.\begin{matrix}C^7H^5O\\Cl\end{matrix}\right\}\right)+\left.\begin{matrix}CN\\Ag\end{matrix}\right\}=\left.\begin{matrix}Ag\\Cl\end{matrix}\right\}+\left(\left.\begin{matrix}C^7H^5O\\CN\end{matrix}\right\}\right)$$

Chloride of benzoyl. Cyanide of silver. Chloride of silver. Cyanide of benzoyl.

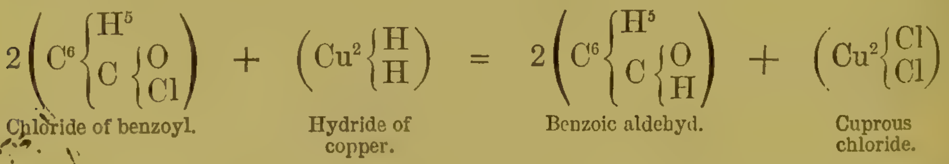


$$\left(\left.\begin{matrix}C^7H^5O\\CN\end{matrix}\right\}\right)+\left.\begin{matrix}H\\H\end{matrix}\right\}=\left(\left.\begin{matrix}CN\\H\end{matrix}\right\}\right)+\left(\left.\begin{matrix}C^7H^5O\\H\end{matrix}\right\}\right)$$

Cyanide of benzoyl. Hydrogen. Hydrocyanic acid. Benzoic aldehyd.

Recently, M. Lippemann has rendered this method still more direct. He has prepared benzoic aldehyd by causing nascent hydrogen disengaged by means of sodium amalgam and a current of perfectly dry gaseous hydrochloric acid to act on the chloride of benzoyl. The hydrochloric acid must be perfectly dry, as the chloride of benzoyl is decomposed by water. This reaction does not succeed either with chloride of acetyl or chloride of succinyl.

We must add that M. Chiozza had long before obtained benzoic aldehyd by the action of the chloride of benzoyl on the hydride of copper, which process, however, yields such a small quantity of the product that it was impossible to collect sufficient for the purpose of analysis:



$$2\left(C^6\left\{\begin{matrix}H^5\\C\left\{\begin{matrix}O\\Cl\end{matrix}\right.\end{matrix}\right.\right)+\left(Cu^2\left\{\begin{matrix}H\\H\end{matrix}\right.\right)=2\left(C^6\left\{\begin{matrix}H^5\\C\left\{\begin{matrix}O\\H\end{matrix}\right.\end{matrix}\right.\right)+\left(Cu^2\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.\right)$$

Chloride of benzoyl. Hydride of copper. Benzoic aldehyd. Cuprous chloride.

In order to be able to ascend the homologous series, it yet remained to transform aldehyds into alcohols. This problem was solved in 1853 by M. Cannizzaro, in the case of the aromatic series. This chemist showed that, in presence of an alcoholic solution of potash, the essential oil of bitter almonds (benzoic aldehyd) is transformed into potassic benzoate and benzoic alcohol:

$$2\left(C^6\left\{\begin{matrix}H^5\\ C\left\{\begin{matrix}O\\ H\end{matrix}\right.\end{matrix}\right.\right) + \left.\begin{matrix}K\\ H\end{matrix}\right\}O = \left(C^6\left\{\begin{matrix}H^5\\ C\left\{\begin{matrix}O\\ OK\end{matrix}\right.\end{matrix}\right.\right) + \left(C^6\left\{\begin{matrix}H^5\\ C\left\{\begin{matrix}H^2\\ OH\end{matrix}\right.\end{matrix}\right.\right)$$

Benzoic aldehyd. Potash. Potassic benzoate. Benzoic alcohol.

Later, in 1856, Kraut found that this reaction is also produced with cuminic aldehyd. But this process was not general: when treated with an alcoholic solution of potash, the fatty aldehyds become resinous without furnishing the least trace of the corresponding alcohol.

In 1861, Fittig somewhat modified this method and rendered it applicable to the series of fatty acids. His modification consists in substituting hydrate of calcium for the alcoholic solution of potash, and he thus succeeded in transforming œnanthylic aldehyd into heptylic alcohol. In 1862, Friedel converted benzoic aldehyd into benzoic alcohol, and M. Wurtz converted ordinary aldehyd into vinic alcohol by means of nascent hydrogen developed by acidulated water and sodium amalgam. Friedel found that this process succeeds with acetones and gives secondary alcohols.

The problem which consisted in ascending from a given term to a higher homologous term was thus solved in the fatty series, but this was not the case in the aromatic series.

M. Cannizzaro having succeeded in preparing an acid presenting the composition $C^8H^8O^2$ by causing an alcoholic solution of potash to act on cyanide of benzoyl, perceived that this acid is not identical, but simply isomeric with Noad's toluic acid obtained by the oxidation of cymene: he moreover found that of these two acids it is that of Noad which is the true homologue of benzoic acid. In reality, this acid furnishes an aldehyd and an alcohol which are analogous in all points to benzoic aldehyd and alcohol, while the acid obtained by means of the cyanide furnishes an aldehyd which has a great tendency to become resinous, and which is never transformed into an alcohol.

In the fatty series, there are several other methods by which, starting from one series, the acid of the higher series can be obtained. One of the most important of these methods is that discovered by Wanklyn in 1858. It consists in preparing a combination of sodium with an alcohol radicle, and causing carbonic anhydride to act on this compound: direct addition takes place, and a sodic salt is formed, from which the acid may then easily be procured:

$$\left(\left.\begin{matrix}C^2H^5\\ Na\end{matrix}\right\}\right) + \left(C\left\{\begin{matrix}O\\ O\end{matrix}\right.\right) = \left(C\left\{\begin{matrix}C^2H^5\\ O\\ ONa\end{matrix}\right.\right)$$

Sodium-ethyl. Carbonic anhydride. Sodic propionate.

$$\left(\left.\begin{matrix}CH^3\\ Na\end{matrix}\right\}\right) + \left(C\left\{\begin{matrix}O\\ O\end{matrix}\right.\right) = \left(C\left\{\begin{matrix}CH^3\\ O\\ ONa\end{matrix}\right.\right)$$

Sodium-methyl. Carbonic anhydride. Sodic acetate.

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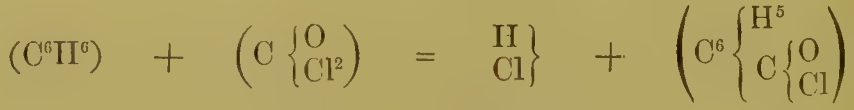
This method appears to be pretty general, especially since Frankland has shown that the sodic compounds of the radicles of all the fatty alcohols may be obtained by submitting to the action of sodium the compounds of these radicles with mercury, which compounds are easily obtained. Frankland's process may perhaps become useful in the aromatic series, in which at present no one has succeeded in combining the alcohol radicles with sodium.

The synthetic method discovered by Wanklyn has not been tried in the aromatic series; but M. Harnitz-Harnitzky discovered one in 1864, in operating on this series; and in 1865 this chemist showed that it also extends to the synthesis of fatty acids, and is generally applicable.

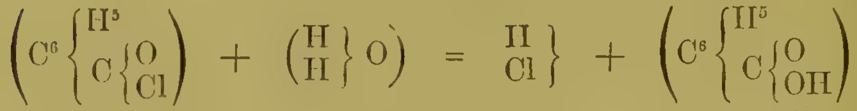
M. Harnitz-Harnitzky's method is founded on the action exercised by the oxychloride of carbon on marsh gas and its homologues, and on benzine and its homologues. In this case double decomposition takes place in which a molecule of hydrochloric acid is produced, while the two residues unite, forming an acid chloride. This chloride, when treated by water, exchanges its chlorine for hydroxyl, and is transformed into the acid sought for:

1st.



$$(C^6H^6) + \left(C\left\{\begin{matrix}O\\Cl^2\end{matrix}\right.\right) = \left.\begin{matrix}H\\Cl\end{matrix}\right\} + \left(C^6\left\{\begin{matrix}H^5\\C\left\{\begin{matrix}O\\Cl\end{matrix}\right.\end{matrix}\right.\right)$$

2nd.

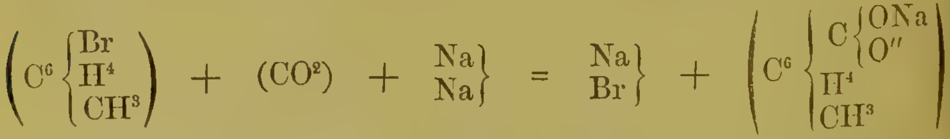


$$\left(C^6\left\{\begin{matrix}H^5\\C\left\{\begin{matrix}O\\Cl\end{matrix}\right.\end{matrix}\right.\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) = \left.\begin{matrix}H\\Cl\end{matrix}\right\} + \left(C^6\left\{\begin{matrix}H^5\\C\left\{\begin{matrix}O\\OH\end{matrix}\right.\end{matrix}\right.\right)$$

M. Harnitz-Harnitzky having only accomplished in the aromatic series the synthesis of benzoic acid, which acid cannot have any isomer, it is not known whether, in the higher series, it would give the true homologues of benzoic acid, or acids identical with those derived from the aromatic hydrocyanic ethers. It is very probable that the latter would be the case.

We did not therefore possess any method by which we could ascend directly from benzoic acid to its true homologues, when M. Kékulé published one in 1866.

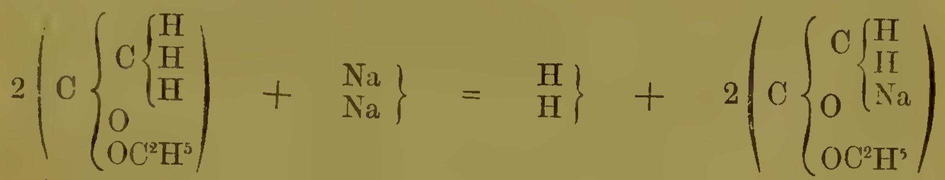
His method consists in causing sodium and carbonic anhydride to act simultaneously with the aid of heat on the monobrominated derivatives, made in the cold, of benzine and its homologues:



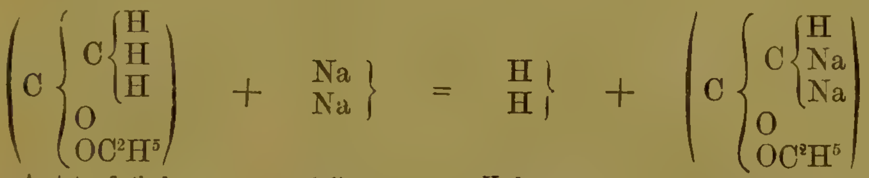
$$\left(C^6\left\{\begin{matrix}Br\\H^4\\CH^3\end{matrix}\right.\right) + (CO^2) + \left.\begin{matrix}Na\\Na\end{matrix}\right\} = \left.\begin{matrix}Na\\Br\end{matrix}\right\} + \left(C^6\left\{\begin{matrix}C\left\{\begin{matrix}ONa\\O''\end{matrix}\right.\\H^4\\CH^3\end{matrix}\right.\right)$$

The results obtained by M. Kékulé will be readily understood if it be borne in mind that in the monobrominated derivatives of the aromatic hydrocarbides made in the cold, the bromine is substituted for the hydrogen of the principal chain ; a natural consequence of this is that the group $CO^2H$ is also substituted for the hydrogen of the principal chain (and this characterizes the true homologues of benzoic acid), instead of being substituted for the hydrogen of a lateral chain, as is the case with the acids obtained by means of the cyanides.

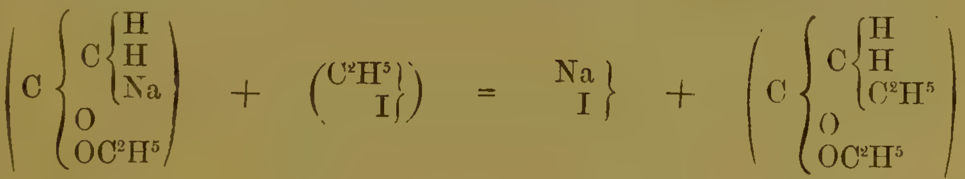
In the course of 1865, Messrs. Frankland and Duppa discovered a very elegant reaction by which acetic acid can be transformed directly into its higher homologues. For this purpose, they cause sodium to act on acetate of ethyl : the sodium is substituted for one or for two atoms of hydrogen of the radicle acetyl, and on causing iodide of methyl or of ethyl to act on the mono- or di-sodic product thus prepared, sodic iodide, and the ethylic ethers of the different acids homologues of acetic acid, are obtained :



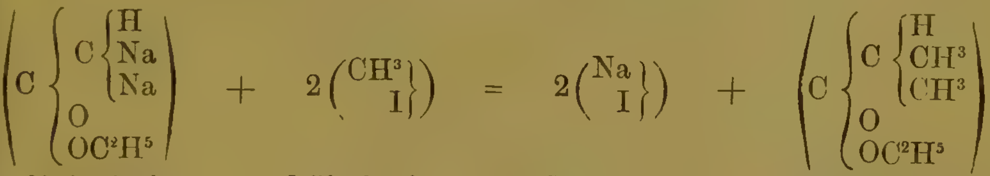
$$2\left(\mathrm{C}\left\{\begin{matrix}\mathrm{C}\left\{\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right.\\\mathrm{O}\\\mathrm{OC^2H^5}\end{matrix}\right.\right) + \left.\begin{matrix}\mathrm{Na}\\\mathrm{Na}\end{matrix}\right\} = \left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\} + 2\left(\mathrm{C}\left\{\begin{matrix}\mathrm{C}\left\{\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{Na}\end{matrix}\right.\\\mathrm{O}\\\mathrm{OC^2H^5}\end{matrix}\right.\right)$$



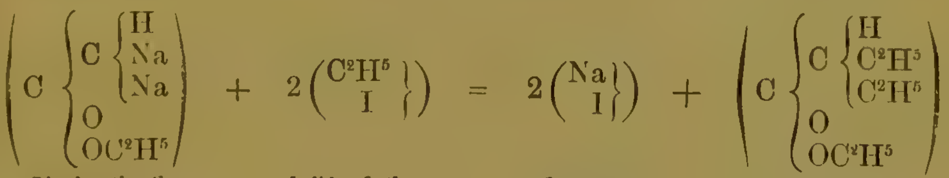
$$\left(\mathrm{C}\left\{\begin{matrix}\mathrm{C}\left\{\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right.\\\mathrm{O}\\\mathrm{OC^2H^5}\end{matrix}\right.\right) + \left.\begin{matrix}\mathrm{Na}\\\mathrm{Na}\end{matrix}\right\} = \left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\} + \left(\mathrm{C}\left\{\begin{matrix}\mathrm{C}\left\{\begin{matrix}\mathrm{H}\\\mathrm{Na}\\\mathrm{Na}\end{matrix}\right.\\\mathrm{O}\\\mathrm{OC^2H^5}\end{matrix}\right.\right)$$



$$\left(\mathrm{C}\left\{\begin{matrix}\mathrm{C}\left\{\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{Na}\end{matrix}\right.\\\mathrm{O}\\\mathrm{OC^2H^5}\end{matrix}\right.\right) + \left(\left.\begin{matrix}\mathrm{C^2H^5}\\\mathrm{I}\end{matrix}\right\}\right) = \left.\begin{matrix}\mathrm{Na}\\\mathrm{I}\end{matrix}\right\} + \left(\mathrm{C}\left\{\begin{matrix}\mathrm{C}\left\{\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{C^2H^5}\end{matrix}\right.\\\mathrm{O}\\\mathrm{OC^2H^5}\end{matrix}\right.\right)$$



$$\left(\mathrm{C}\left\{\begin{matrix}\mathrm{C}\left\{\begin{matrix}\mathrm{H}\\\mathrm{Na}\\\mathrm{Na}\end{matrix}\right.\\\mathrm{O}\\\mathrm{OC^2H^5}\end{matrix}\right.\right) + 2\left(\left.\begin{matrix}\mathrm{CH^3}\\\mathrm{I}\end{matrix}\right\}\right) = 2\left(\left.\begin{matrix}\mathrm{Na}\\\mathrm{I}\end{matrix}\right\}\right) + \left(\mathrm{C}\left\{\begin{matrix}\mathrm{C}\left\{\begin{matrix}\mathrm{H}\\\mathrm{CH^3}\\\mathrm{CH^3}\end{matrix}\right.\\\mathrm{O}\\\mathrm{OC^2H^5}\end{matrix}\right.\right)$$



$$\left(\mathrm{C}\left\{\begin{matrix}\mathrm{C}\left\{\begin{matrix}\mathrm{H}\\\mathrm{Na}\\\mathrm{Na}\end{matrix}\right.\\\mathrm{O}\\\mathrm{OC^2H^5}\end{matrix}\right.\right) + 2\left(\left.\begin{matrix}\mathrm{C^2H^5}\\\mathrm{I}\end{matrix}\right\}\right) = 2\left(\left.\begin{matrix}\mathrm{Na}\\\mathrm{I}\end{matrix}\right\}\right) + \left(\mathrm{C}\left\{\begin{matrix}\mathrm{C}\left\{\begin{matrix}\mathrm{H}\\\mathrm{C^2H^5}\\\mathrm{C^2H^5}\end{matrix}\right.\\\mathrm{O}\\\mathrm{OC^2H^5}\end{matrix}\right.\right)$$

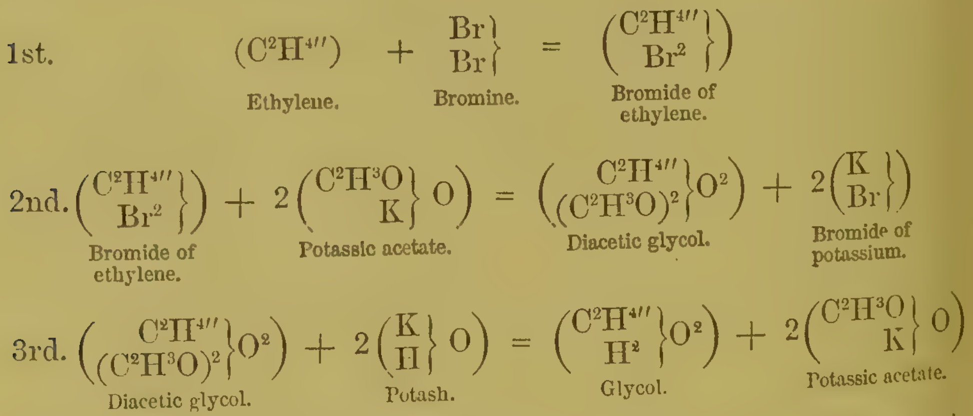
It will be seen that acids of the same centesimal composition are formed whether one atom of ethyl be substituted for one of hydrogen, or two of methyl for two of hydrogen, in acetic ether. It is very probable that these acids are only isomers, and this is an interesting question which Dr. Frankland proposes to decide, hoping also to be able to generalise his process by employing it in the aromatic series.

So far we have seen in what manner the synthesis of monatomic hydrocarbides, alcohols, aldehyds, and acids is accomplished, but we have not yet spoken of the synthesis of polyatomic compounds.

We may imagine two synthetic methods for these, one of which would consist in preparing the polyatomic compounds of a series by means of the monatomic compounds of the same series; the second, on the contrary, would consist in preparing the polyatomic compounds of a series by means of the polyatomic compounds of a lower series. Processes exist corresponding to each of these methods. But if we wish to ascend a homologous series from one end to the other, it is always necessary to use the monatomic compounds. Without this, in the series of the fatty acids at least, the synthesis is interrupted, as it is not yet known how to pass from a polyatomic acid of this series to the corresponding alcohol.

Biatomic alcohols have only as yet been prepared in the fatty series: two synthetic processes may be used to obtain them.

The most important of these was discovered by Wurtz in 1859, and consists in combining ethylene or one of its homologues with bromine or iodine, and then causing acetate of silver or of potassium to act on the bromide or iodide thus obtained: two atoms of oxacetyl are then substituted for two atoms of the halogen metalloid, and a diacetic ether is thereby formed, which, when saponified by a base, furnishes the biatomic alcohol sought for:



1st. $$(C^2H^{4\prime\prime}) + \left.\begin{matrix}Br\\Br\end{matrix}\right\} = \left(\left.\begin{matrix}C^2H^{4\prime\prime}\\Br^2\end{matrix}\right\}\right)$$

Ethylene. Bromine. Bromide of ethylene.

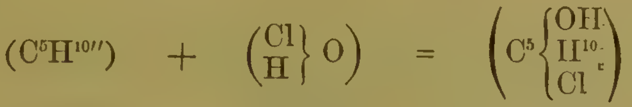
2nd. $$\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\Br^2\end{matrix}\right\}\right) + 2\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}C^2H^{4\prime\prime}\\(C^2H^3O)^2\end{matrix}\right\}O^2\right) + 2\left(\left.\begin{matrix}K\\Br\end{matrix}\right\}\right)$$

Bromide of ethylene. Potassic acetate. Diacetic glycol. Bromide of potassium.

3rd. $$\left(\left.\begin{matrix}C^2H^{4\prime\prime}\\(C^2H^3O)^2\end{matrix}\right\}O^2\right) + 2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}C^2H^{4\prime\prime}\\H^2\end{matrix}\right\}O^2\right) + 2\left(\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O\right)$$

Diacetic glycol. Potash. Glycol. Potassic acetate.

The second process of preparing glycols synthetically is owing to M. Carius, and dates from 1863. It is based on the fact that ethylene and its homologues unite directly with hypochlorous acid, giving a chlorhydrin of the glycol which corresponds to them. This monochlorhydrin, when submitted successively to the actions of acetate of silver and of alkalies, gives the glycol sought for:

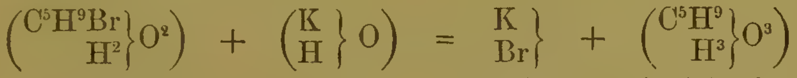


$$(C^5H^{10''}) + \left(\left.\begin{matrix}Cl\\H\end{matrix}\right\}O\right) = \left(C^5\left\{\begin{matrix}OH\\H^{10}\\Cl\end{matrix}\right.\right)$$

Amylene. Hypochlorous acid. Amylenic chlorhydrin.

The synthesis of the glycols is therefore bound up with that of ethylene and its homologues, and though, as an exceptional case, M. Caventou has succeeded in preparing ordinary glycol by substituting bromide of brominated ethyl for the bromide of ethylene, generally speaking, we may affirm that, where the hydrocarbides are unknown, so are the glycols. Now as these hydrocarbides which are obtained so easily in the fatty series by submitting monatomic alcohols to dehydrating actions have never been prepared in the aromatic series, neither have the glycols of this series been obtained.

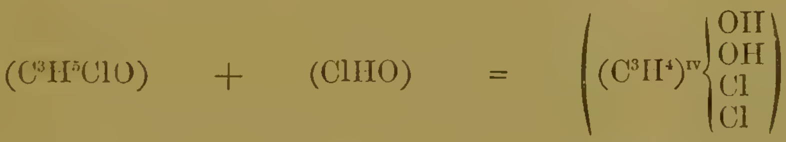
Triatomic alcohols have not as yet been obtained synthetically, with the exception of amyl-glycerine which was discovered by M. Baüer in 1861. In order to prepare it, this chemist heated bromide of brominated amylene with two molecules of acetate of silver, and then saponified the product of the reaction by means of caustic potash; the body which results from this is monobrominated amyl-glycol. This body, heated with an excess of potash, exchanges its bromine for hydroxyl and is converted into amyl-glycerine:



$$\left(\left.\begin{matrix}C^5H^9Br\\H^2\end{matrix}\right\}O^2\right) + \left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right) = \left.\begin{matrix}K\\Br\end{matrix}\right\} + \left(\left.\begin{matrix}C^5H^9\\H^3\end{matrix}\right\}O^3\right)$$

Monobrominated amyl-glycol. Potash. Bromide of potassium. Amyl-glycerine.

The synthesis of only one alcohol of an atomicity greater than three has been accomplished. This is the tetratomic alcohol corresponding to the formula ($C^3H^8O^4$). It was discovered in 1865 by Carius, who called it propyl-phycite, and in order to prepare it he caused hypochlorous acid to act on glyceric epichlorhydrin; these two bodies combine, giving a dichlorhydrin of propyl-phycite: he then prepared the alcohol by means of this dichlorhydrin by the same process as that used to obtain the glycols by means of their dibromhydrins; the following equation explains this synthesis:



$$(C^3H^5ClO) + (ClHO) = \left((C^3H^4)^{iv}\left\{\begin{matrix}OH\\OH\\Cl\\Cl\end{matrix}\right.\right)$$

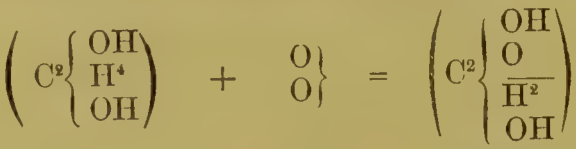
Glyceric epichlorhydrin. Hypochlorous acid. Dichlorhydric propyl-phycite.

The synthesis of polyatomic acids is more advanced than that of alcohols of the same atomicity. We will first speak of biatomic acids.

These acids are divided into two classes; one comprising those which contain an alcoholic residue of water and an acid residue of water, and into whose molecule there enter three atoms of oxygen; the second comprising those which contain four atoms of oxygen, and two atoms of hydroxyl, both acid, that is to say, united to carbonyl CO. Glycolic acid ($C^2H^4O^3$) and lactic acid ($C^3H^6O^3$) may be taken as examples of the first class; and oxalic acid ($C^2H^2O^4$) and succinic acid ($C^4H^6O^4$) as those of the second.

Acids of the first class, that is to say, biatomic and monobasic acids, may be prepared: 1st, by means of the corresponding glycols; 2nd, by means of the monatomic acids from which they only differ by an atom of oxygen; 3rd, by employing the glycols which contain $CH^2$ less than themselves; 4th, by using hydrocarbides analogous to ethylene; 5th, by using aldehyds derived from monatomic alcohols; 6th, by means of oxalic acid; 7th, in the aromatic series by means of monatomic phenols.

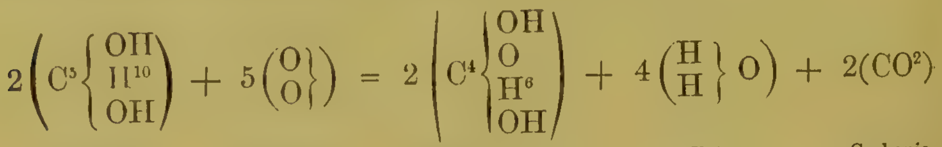
We owe the first of these processes to M. Wurtz, who in 1859 discovered that, under the influence of platinum black, ordinary glycol gives glycolic acid, and propyl-glycol gives lactic acid:



$$\left(C^2\left\{\begin{matrix}OH\\H^4\\OH\end{matrix}\right.\right) + \left.\begin{matrix}O\\O\end{matrix}\right\} = \left(C^2\left\{\begin{matrix}OH\\O\\\overline{H^2}\\OH\end{matrix}\right.\right)$$

Glycol. Oxygen. Glycolic acid.

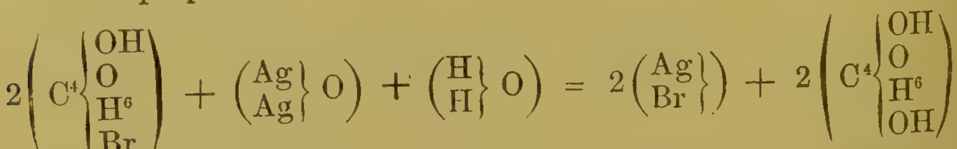
However, with glycols which are richer in carbon than propyl-glycol the oxidation does not take place so regularly: part of the carbon and hydrogen separate entirely from the group, and instead of the acid desired, a lower homologue of this acid is produced:



$$2\left(C^5\left\{\begin{matrix}OH\\H^{10}\\OH\end{matrix}\right.\right) + 5\left(\left.\begin{matrix}O\\O\end{matrix}\right\}\right) = 2\left(C^4\left\{\begin{matrix}OH\\O\\H^6\\OH\end{matrix}\right.\right) + 4\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + 2(CO^2)$$

Amyl-glycol. Oxygen. Butylactic acid. Water. Carbonic anhydride.

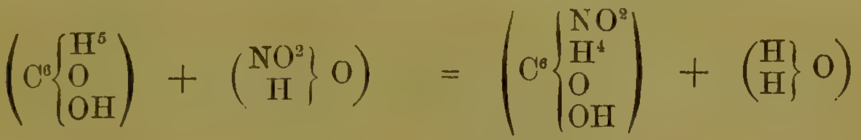
The second process, discovered by Hofmann and Kékulé, consists in preparing the monobrominated derivatives of monatomic acids, and boiling them with water and oxide of silver: bromide of silver is produced, and an acid which contains an atom more oxygen than that used for its preparation:



$$2\left(C^4\left\{\begin{matrix}OH\\O\\H^6\\Br\end{matrix}\right.\right) + \left(\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) = 2\left(\left.\begin{matrix}Ag\\Br\end{matrix}\right\}\right) + 2\left(C^4\left\{\begin{matrix}OH\\O\\H^6\\OH\end{matrix}\right.\right)$$

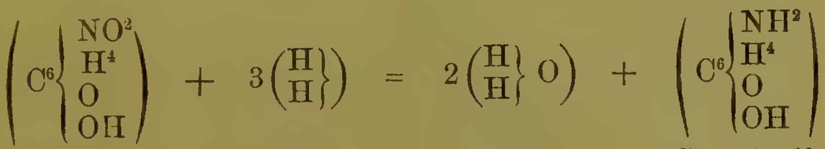
Bromobutyric acid. Oxide of silver. Water. Bromide of silver. Oxybutyric acid.

In the aromatic series, monatomic acids may be transformed into biatomic monobasic acids, by preparing the mononitrous derivatives of the first of these acids, reducing these derivatives by nascent hydrogen, and submitting the amide thus formed to the action of nitrous acid:



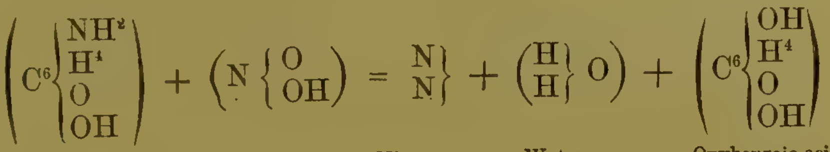
$$\left(C^6\left\{\begin{array}{l}H^5\\O\\OH\end{array}\right.\right) + \left(\left.\begin{array}{l}NO^2\\H\end{array}\right\}O\right) = \left(C^6\left\{\begin{array}{l}NO^2\\H^4\\O\\OH\end{array}\right.\right) + \left(\left.\begin{array}{l}H\\H\end{array}\right\}O\right)$$

Benzoic acid. Nitric acid. Nitrobenzoic acid. Water.



$$\left(C^6\left\{\begin{array}{l}NO^2\\H^4\\O\\OH\end{array}\right.\right) + 3\left(\left.\begin{array}{l}H\\H\end{array}\right\}\right) = 2\left(\left.\begin{array}{l}H\\H\end{array}\right\}O\right) + \left(C^6\left\{\begin{array}{l}NH^2\\H^4\\O\\OH\end{array}\right.\right)$$

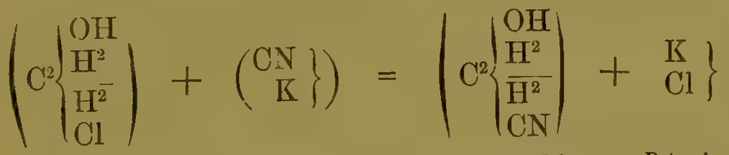
Nitrobenzoic acid. Hydrogen. Water. Benzamic acid.



$$\left(C^6\left\{\begin{array}{l}NH^2\\H^4\\O\\OH\end{array}\right.\right) + \left(N\left\{\begin{array}{l}O\\OH\end{array}\right.\right) = \left.\begin{array}{l}N\\N\end{array}\right\} + \left(\left.\begin{array}{l}H\\H\end{array}\right\}O\right) + \left(C^6\left\{\begin{array}{l}OH\\H^4\\O\\OH\end{array}\right.\right)$$

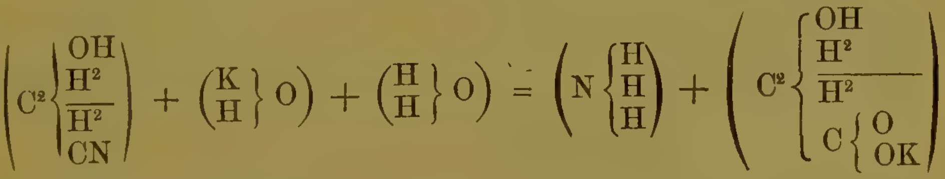
Benzamic acid. Nitrous acid. Nitrogen. Water. Oxybenzoic acid.

The third process was first employed by Wislicenus in 1863. It consists in preparing the monocyanhydrin of a glycol by means of the monochlorhydrin of the same body and cyanide of silver, and then causing this monocyanhydrin to react when hot on potassic hydrate dissolved in alcohol; the reaction is the same as that in which the cyanide of monatomic alcohol radicles are transformed into monatomic acids:



$$\left(C^2\left\{\begin{array}{l}OH\\H^2\\\hline H^2\\Cl\end{array}\right.\right) + \left(\left.\begin{array}{l}CN\\K\end{array}\right\}\right) = \left(C^2\left\{\begin{array}{l}OH\\H^2\\\hline H^2\\CN\end{array}\right.\right) + \left.\begin{array}{l}K\\Cl\end{array}\right\}$$

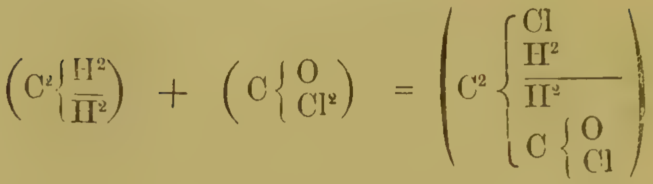
Monochlorhydrin of glycol. Cyanide of potassium. Monocyanhydrin of glycol. Potassic chloride.



$$\left(C^2\left\{\begin{array}{l}OH\\H^2\\\hline H^2\\CN\end{array}\right.\right) + \left(\left.\begin{array}{l}K\\H\end{array}\right\}O\right) + \left(\left.\begin{array}{l}H\\H\end{array}\right\}O\right) = \left(N\left\{\begin{array}{l}H\\H\\H\end{array}\right.\right) + \left(C^2\left\{\begin{array}{l}OH\\H^2\\\hline H^2\\C\left\{\begin{array}{l}O\\OK\end{array}\right.\end{array}\right.\right)$$

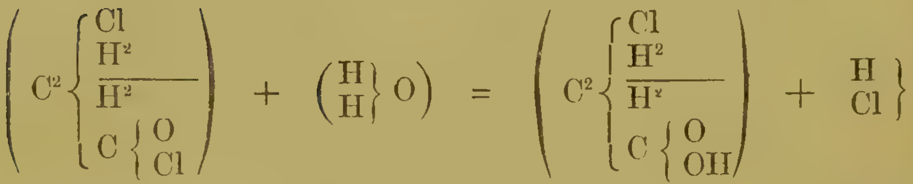
Monocyanhydrin of glycol. Potassic hydrate. Water. Ammonia. Potassic lactate.

In the fourth process, which was discovered by M. Lippemann in 1863, the direct combination which takes place when ethylene or its homologues react on the oxychloride of carbon is made use of. In this reaction there is formed the bichloride of the radicle of a biatomic and monobasic acid of the series higher than that of which the hydrocarbide employed forms part. We know that, by water, bichlorides are converted into hydrochloric acid and a monochlorinated monatomic acid, which, when acted upon by potash, or by water and oxide of silver, furnishes the biatomic acid desired:



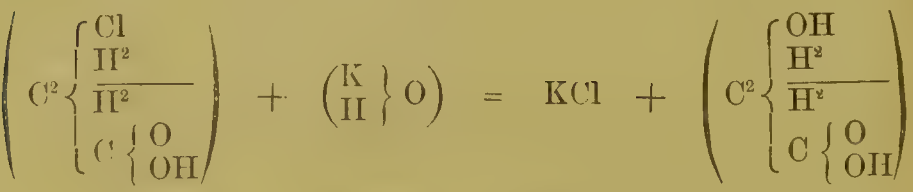
$$\left(C^2\left\{\begin{array}{l}H^2\\ \hline H^2\end{array}\right.\right) + \left(C\left\{\begin{array}{l}O\\ Cl^2\end{array}\right.\right) = \left(C^2\left\{\begin{array}{l}Cl\\ H^2\\ \hline H^2\\ C\left\{\begin{array}{l}O\\ Cl\end{array}\right.\end{array}\right.\right)$$

Ethylene. Oxychloride of carbon. Chloride of lactyl.



$$\left(C^2\left\{\begin{array}{l}Cl\\ H^2\\ \hline H^2\\ C\left\{\begin{array}{l}O\\ Cl\end{array}\right.\end{array}\right.\right) + \left(\begin{array}{l}H\\ H\end{array}\right\}O\Big) = \left(C^2\left\{\begin{array}{l}Cl\\ H^2\\ \hline H^2\\ C\left\{\begin{array}{l}O\\ OH\end{array}\right.\end{array}\right.\right) + \left.\begin{array}{l}H\\ Cl\end{array}\right\}$$

Chloride of lactyl. Water. Chloropropionic acid. Hydrochloric acid.

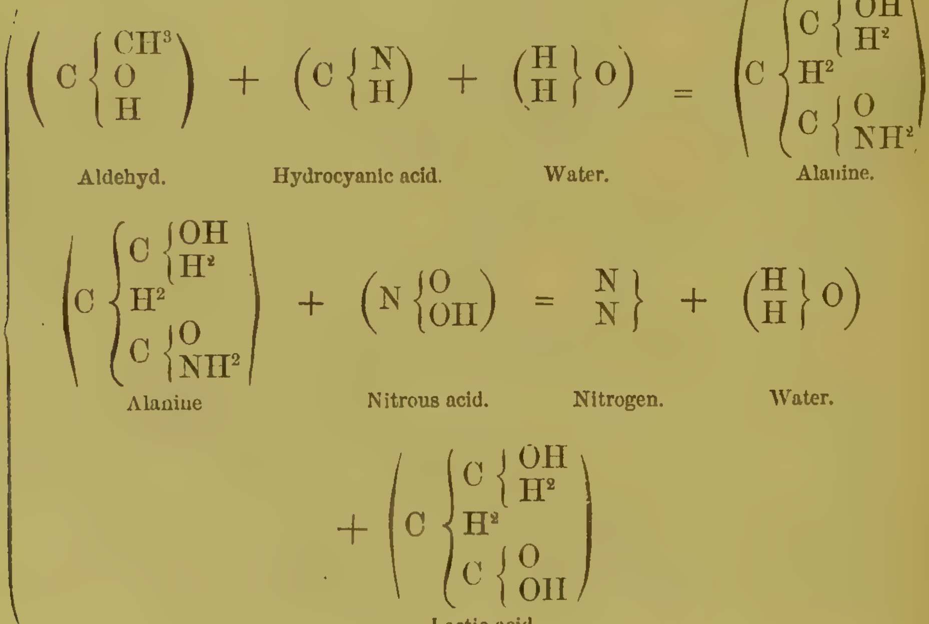


$$\left(C^2\left\{\begin{array}{l}Cl\\ H^2\\ \hline H^2\\ C\left\{\begin{array}{l}O\\ OH\end{array}\right.\end{array}\right.\right) + \left(\begin{array}{l}K\\ H\end{array}\right\}O\Big) = KCl + \left(C^2\left\{\begin{array}{l}OH\\ H^2\\ \hline H^2\\ C\left\{\begin{array}{l}O\\ OH\end{array}\right.\end{array}\right.\right)$$

Chloropropionic acid. Potash. Chloride of potassium. Lactic acid.

The fifth process, which has long been known, consists in leaving to itself a mixture of an aldehyd corresponding to a monatomic acid, hydrocyanic acid and water, to which a little hydrochloric acid must be added to facilitate the reaction. In this case, sometimes an amide is produced, which nitrous acid transforms into one of the acids in question, and sometimes this acid is directly formed :

1st.



$$\left(C\left\{\begin{array}{l}CH^3\\ O\\ H\end{array}\right.\right) + \left(C\left\{\begin{array}{l}N\\ H\end{array}\right.\right) + \left(\begin{array}{l}H\\ H\end{array}\right\}O\Big) = \left(C\left\{\begin{array}{l}C\left\{\begin{array}{l}OH\\ H^2\end{array}\right.\\ H^2\\ C\left\{\begin{array}{l}O\\ NH^2\end{array}\right.\end{array}\right.\right)$$

Aldehyd. Hydrocyanic acid. Water. Alanine.

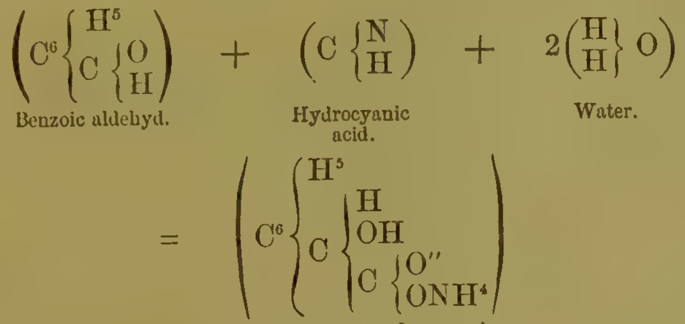
$$\left(C\left\{\begin{array}{l}C\left\{\begin{array}{l}OH\\ H^2\end{array}\right.\\ H^2\\ C\left\{\begin{array}{l}O\\ NH^2\end{array}\right.\end{array}\right.\right) + \left(N\left\{\begin{array}{l}O\\ OH\end{array}\right.\right) = \left.\begin{array}{l}N\\ N\end{array}\right\} + \left(\begin{array}{l}H\\ H\end{array}\right\}O\Big)$$

Alanine. Nitrous acid. Nitrogen. Water.

$$+ \left(C\left\{\begin{array}{l}C\left\{\begin{array}{l}OH\\ H^2\end{array}\right.\\ H^2\\ C\left\{\begin{array}{l}O\\ OH\end{array}\right.\end{array}\right.\right)$$

Lactic acid.

2nd.



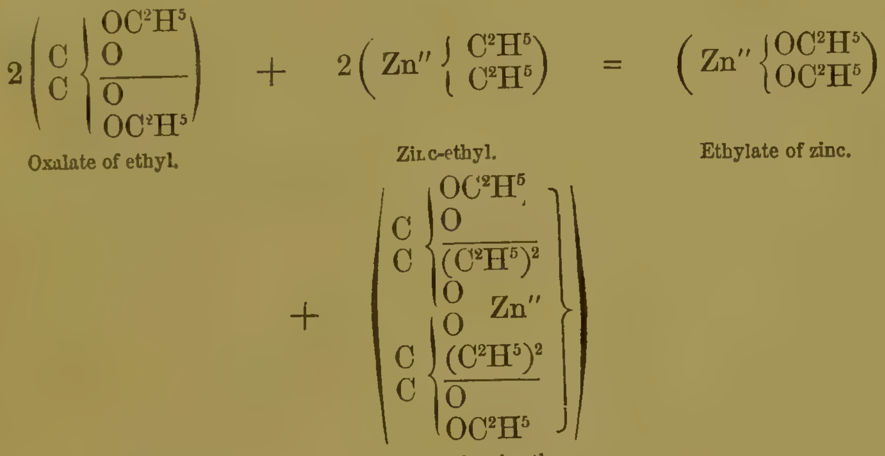
$$\left(C^6\left\{\begin{matrix}H^5\\ C\left\{\begin{matrix}O\\H\end{matrix}\right.\end{matrix}\right.\right) + \left(C\left\{\begin{matrix}N\\H\end{matrix}\right.\right) + 2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)$$

Benzoic aldehyd. Hydrocyanic acid. Water.

$$= \left(C^6\left\{\begin{matrix}H^5\\ C\left\{\begin{matrix}H\\OH\\ C\left\{\begin{matrix}O''\\ONH^4\end{matrix}\right.\end{matrix}\right.\end{matrix}\right.\right)$$

Formobenzoate of ammonium.

The sixth process was discovered by Frankland in 1863, and consists in the substitution of radicles of alcohols for part of the oxygen which is directly united to carbon in oxalic acid. To effect this, zinc-ethyl or zinc-methyl is made to act on diethylic oxalate; a zinco-ethylic leucate is thus formed, which, when treated by water, gives leucate of ethyl and hydrate of zinc:

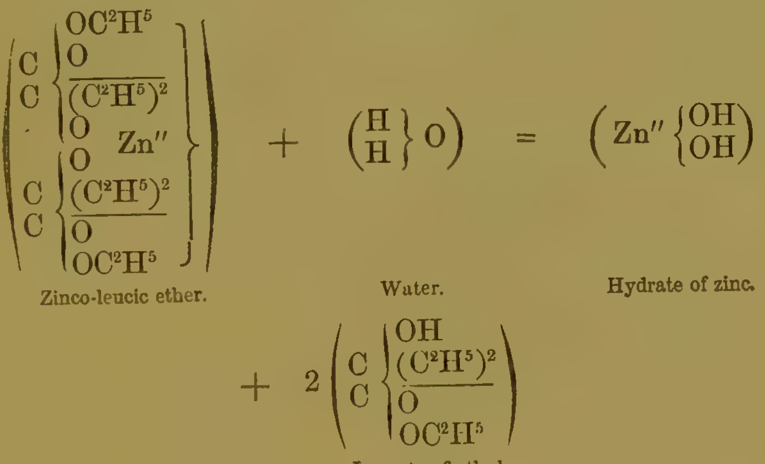


$$2\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}OC^2H^5\\O\\\hline O\\OC^2H^5\end{array}\right.\right) + 2\left(Zn''\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right.\right) = \left(Zn''\left\{\begin{matrix}OC^2H^5\\OC^2H^5\end{matrix}\right.\right)$$

Oxalate of ethyl. Zinc-ethyl. Ethylate of zinc.

$$+\left(\left.\begin{array}{l}\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}OC^2H^5\\O\\\hline (C^2H^5)^2\\O\end{array}\right.\\ \qquad\qquad Zn''\\ \begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}O\\(C^2H^5)^2\\\hline O\\OC^2H^5\end{array}\right.\end{array}\right\}\right)$$

Zinco-leucic ether.



$$\left(\left.\begin{array}{l}\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}OC^2H^5\\O\\\hline (C^2H^5)^2\\O\end{array}\right.\\ \qquad\qquad Zn''\\ \begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}O\\(C^2H^5)^2\\\hline O\\OC^2H^5\end{array}\right.\end{array}\right\}\right) + \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) = \left(Zn''\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)$$

Zinco-leucic ether. Water. Hydrate of zinc.

$$+\ 2\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}OH\\(C^2H^5)^2\\\hline O\\OC^2H^5\end{array}\right.\right)$$

Leucate of ethyl.

The leucate of ethyl being then saponified by means of hydrate of barium, furnishes alcohol and leucic acid.

Instead of preparing the zinc-methyl separately, it is more convenient to cause zinc in powder, and iodide of methyl or of ethyl, to act simultaneously on oxalic ether. If, instead of using iodide of ethyl or of methyl, a mixture of these two ethers be employed, etho-methoxalic acid is obtained, that is to say, oxalic acid in which an atom of oxygen is replaced by an atom of methyl and one of ethyl.

It is scarcely probable that the acids thus prepared are identical with those obtained by other methods.

The first four and the sixth processes have as yet been employed exclusively in the series of the fatty acids; the fifth is general. The seventh process can only be applied to the aromatic series: Kolbe, in 1860, was the first to employ it. It consists in causing carbonic anhydride and sodium to act simultaneously on a phenol: the sodium is substituted for the hydrogen of the phenol, and the carbonic anhydride is fixed on the sodic phenate thus produced. A sodic salt is thereby formed, by means of which the desired acid is easily prepared:

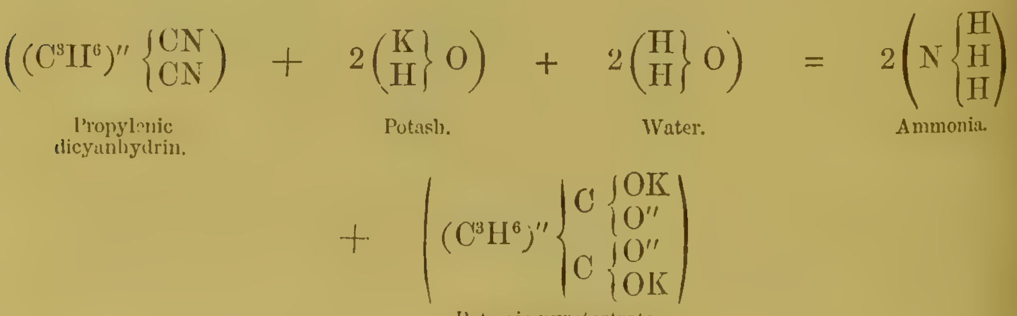
$$\underset{\text{Thymate of sodium.}}{(C^{10}H^{13}NaO)} + \underset{\text{Carbonic anhydride.}}{(CO^2)} = \underset{\text{Thymotate of sodium.}}{(C^{11}H^{13}NaO^3)}$$

The acids obtained by this last method contain phenic hydroxyl instead of the alcoholic hydroxyl contained in those prepared by the other methods.

The synthesis of biatomic and bibasic acids is much less advanced: it has been accomplished in the fatty series, and that only by three methods, the first of which was discovered by M. Wurtz, and consists in oxidizing glycol by nitric acid. This alcohol then exchanges $H^4$ for $O^2$, and is converted into oxalic acid. Unfortunately, this degree of oxidation is always exceeded when, instead of ordinary glycol, another glycol is used. Instead of a homologue of oxalic acid, this acid itself is again obtained, along with the products of complete combustion, such as water and carbonic anhydride. This method therefore can be employed for the synthesis of oxalic acid only.

In the second method, discoved by Maxwell Simpson in 1860, the dicyanhydrin of a glycol is heated with caustic potash; ammonia is disengaged, and the dipotassic salt of the acid sought for is formed. The acid thus prepared belongs to a series higher by two terms than that of which the dicyanhydrin employed formed a part.

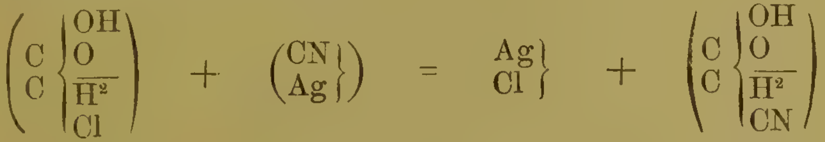
The dicyanhydrins intended for these syntheses are prepared by heating the dibromhydrins with an alcoholic solution of potassic cyanide:



$$\underset{\text{Propylenic dicyanhydrin.}}{\left((C^3H^6)''\left\{\begin{matrix}CN\\CN\end{matrix}\right.\right)} + \underset{\text{Potash.}}{2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right)} + \underset{\text{Water.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Ammonia.}}{2\left(N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.\right)}$$

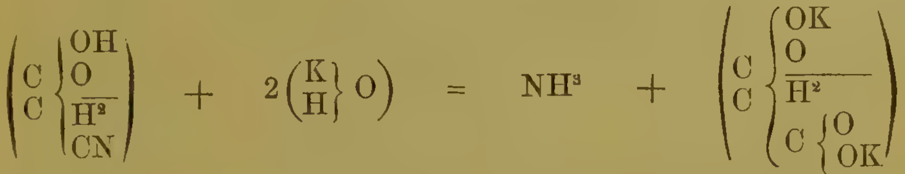
$$+ \underset{\text{Potassic pyrotartrate.}}{\left((C^3H^6)''\left\{\begin{matrix}C\left\{\begin{matrix}OK\\O''\end{matrix}\right.\\C\left\{\begin{matrix}O''\\OK\end{matrix}\right.\end{matrix}\right.\right)}$$

The third method, which will probably become general, is due to Kolbe and Mulher, who both discovered it at the same time. These chemists used it in 1863 to prepare malonic acid. To effect this, they heated chloracetic acid with cyanide of silver, whereby cyanacetic acid was formed, which, when boiled with potash, was converted into potassic malonate and ammonia:



$$\left(\begin{array}{l}\mathrm{C}\\ \mathrm{C}\end{array}\left\{\begin{array}{l}\mathrm{OH}\\ \mathrm{O}\\ \hline \mathrm{H^2}\\ \mathrm{Cl}\end{array}\right.\right) + \left(\left.\begin{array}{l}\mathrm{CN}\\ \mathrm{Ag}\end{array}\right\}\right) = \left.\begin{array}{l}\mathrm{Ag}\\ \mathrm{Cl}\end{array}\right\} + \left(\begin{array}{l}\mathrm{C}\\ \mathrm{C}\end{array}\left\{\begin{array}{l}\mathrm{OH}\\ \mathrm{O}\\ \hline \mathrm{H^2}\\ \mathrm{CN}\end{array}\right.\right)$$

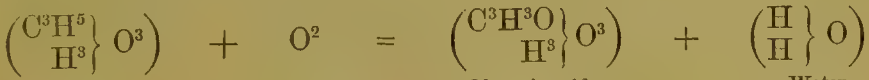
Chloracetic acid. Cyanide of silver. Chloride of silver. Cyanacetic acid.



$$\left(\begin{array}{l}\mathrm{C}\\ \mathrm{C}\end{array}\left\{\begin{array}{l}\mathrm{OH}\\ \mathrm{O}\\ \hline \mathrm{H^2}\\ \mathrm{CN}\end{array}\right.\right) + 2\left(\left.\begin{array}{l}\mathrm{K}\\ \mathrm{H}\end{array}\right\}\mathrm{O}\right) = \mathrm{NH^3} + \left(\begin{array}{l}\mathrm{C}\\ \mathrm{C}\end{array}\left\{\begin{array}{l}\mathrm{OK}\\ \mathrm{O}\\ \hline \mathrm{H^2}\\ \mathrm{C}\left\{\begin{array}{l}\mathrm{O}\\ \mathrm{OK}\end{array}\right.\end{array}\right.\right)$$

Cyanacetic acid. Potassic hydrate. Ammonia. Potassic malonate.

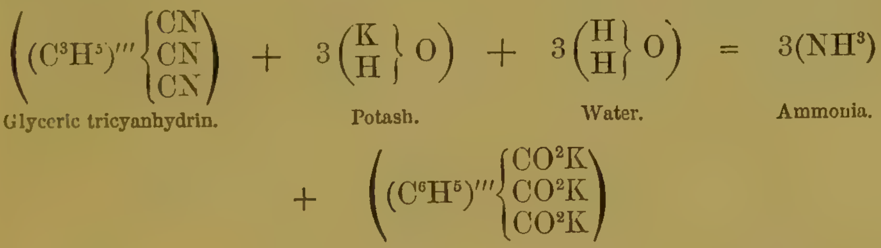
The triatomic acids which correspond to the glycerines are very little known; one of them, glyceric acid, has been obtained by Debus, by oxidizing glycerine with nitric acid:



$$\left(\left.\begin{array}{r}\mathrm{C^3H^5}\\ \mathrm{H^3}\end{array}\right\}\mathrm{O^3}\right) + \mathrm{O^2} = \left(\left.\begin{array}{r}\mathrm{C^3H^3O}\\ \mathrm{H^3}\end{array}\right\}\mathrm{O^3}\right) + \left(\left.\begin{array}{l}\mathrm{H}\\ \mathrm{H}\end{array}\right\}\mathrm{O}\right)$$

Glycerine. Oxygen. Glyceric acid. Water.

A triatomic and tribasic acid, carballylic acid, answering to the formula $C^6H^8O^6$, has been prepared by Maxwell Simpson, by means of glyceric tricyanhydrin and alkalies:



$$\left((\mathrm{C^3H^5})'''\left\{\begin{array}{l}\mathrm{CN}\\ \mathrm{CN}\\ \mathrm{CN}\end{array}\right.\right) + 3\left(\left.\begin{array}{l}\mathrm{K}\\ \mathrm{H}\end{array}\right\}\mathrm{O}\right) + 3\left(\left.\begin{array}{l}\mathrm{H}\\ \mathrm{H}\end{array}\right\}\mathrm{O}\right) = 3(\mathrm{NH^3})$$

Glyceric tricyanhydrin. Potash. Water. Ammonia.

$$+ \left((\mathrm{C^6H^5})'''\left\{\begin{array}{l}\mathrm{CO^2K}\\ \mathrm{CO^2K}\\ \mathrm{CO^2K}\end{array}\right.\right)$$

Carballylate of potassium.

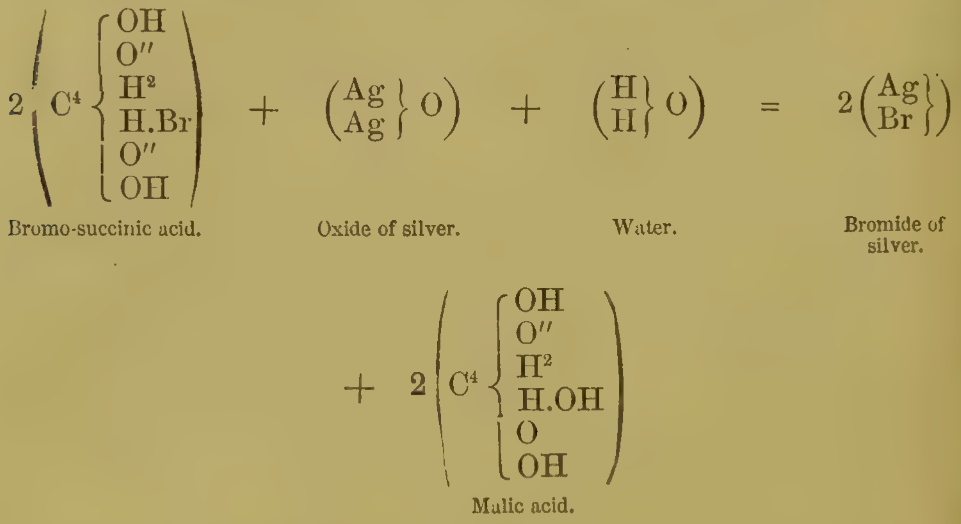
Besides this, triatomic and monobasic acids may be obtained by the action of moist oxide of silver on the bichlorinated or bibrominated derivatives of monatomic acids, at least it may be so deduced from the experiments of MM. Friedel and Machuca, who have succeeded in preparing dioxybutyric acid by this means:

$$(\mathrm{C^4H^6Br^2O^2}) + \mathrm{Ag^2O} + \mathrm{H^2O} = 2(\mathrm{AgBr}) + (\mathrm{C^4H^8O^4})$$

Dibromo-butyric acid. Oxide of silver. Water. Bromide of silver. Dioxybutyric acid.

Lastly, malic acid, which is triatomic and bibasic, was prepared in

1860 by Kékulé on one hand, and by Perkin and Duppa on the other, by means of bromo-succinic acid and moist oxide of silver:

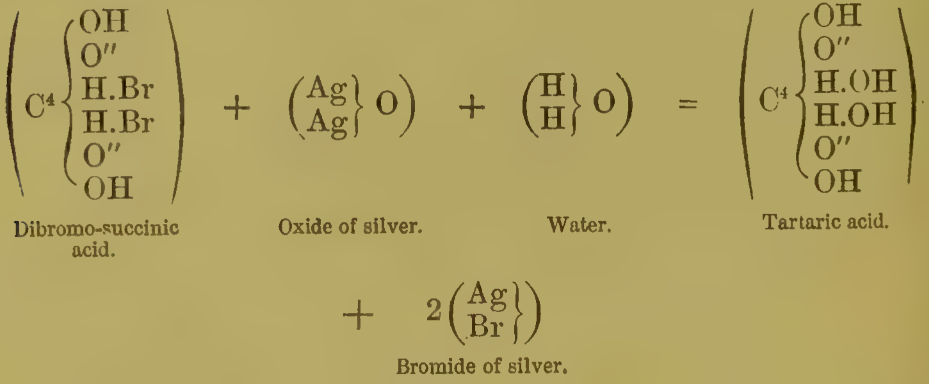


$$2\left(C^4\left\{\begin{array}{l}OH\\O''\\H^2\\H.Br\\O''\\OH\end{array}\right.\right) + \left(\begin{array}{l}Ag\\Ag\end{array}\right\}O\Big) + \left(\begin{array}{l}H\\H\end{array}\right\}O\Big) = 2\left(\begin{array}{l}Ag\\Br\end{array}\right\}\Big) + 2\left(C^4\left\{\begin{array}{l}OH\\O''\\H^2\\H.OH\\O\\OH\end{array}\right.\right)$$

Bromo-succinic acid. Oxide of silver. Water. Bromide of silver.

Malic acid.

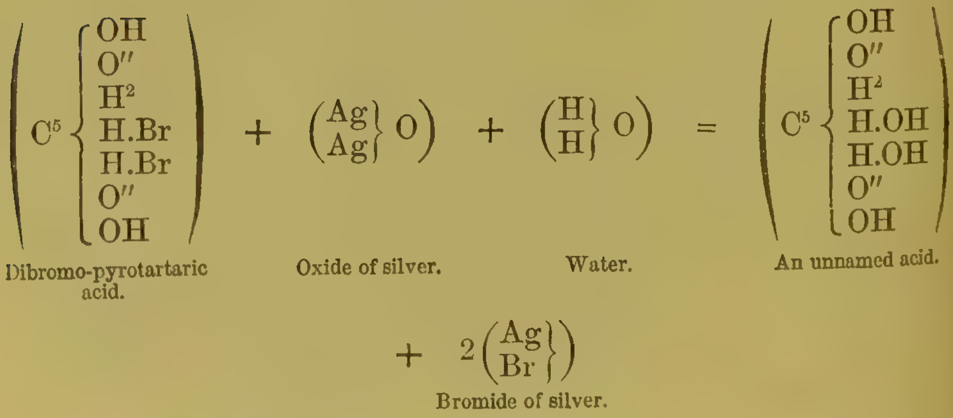
It is known that there are very few acids in existence having an atomicity greater than three, and that the best known of these are tartaric acid $C^4H^6O^6$, a homologue of this latter hitherto unnamed $C^5H^8O^6$, citric acid $C^6H^8O^7$, and gallic acid $C^7H^6O^5$. With the exception of citric acid, all these have been obtained synthetically: tartaric acid and its homologue result from the action of oxide of silver on dibromo-succinic and dibromo-pyrotartaric acids, and gallic acid is produced when dibromo-salicylic acid is treated in the same manner:



$$\left(C^4\left\{\begin{array}{l}OH\\O''\\H.Br\\H.Br\\O''\\OH\end{array}\right.\right) + \left(\begin{array}{l}Ag\\Ag\end{array}\right\}O\Big) + \left(\begin{array}{l}H\\H\end{array}\right\}O\Big) = \left(C^4\left\{\begin{array}{l}OH\\O''\\H.OH\\H.OH\\O''\\OH\end{array}\right.\right) + 2\left(\begin{array}{l}Ag\\Br\end{array}\right\}\Big)$$

Dibromo-succinic acid. Oxide of silver. Water. Tartaric acid.

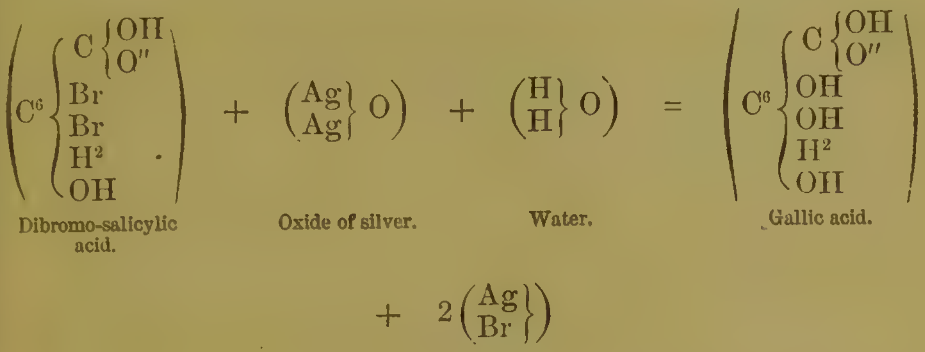
Bromide of silver.



$$\left(C^5\left\{\begin{array}{l}OH\\O''\\H^2\\H.Br\\H.Br\\O''\\OH\end{array}\right.\right) + \left(\begin{array}{l}Ag\\Ag\end{array}\right\}O\Big) + \left(\begin{array}{l}H\\H\end{array}\right\}O\Big) = \left(C^5\left\{\begin{array}{l}OH\\O''\\H^2\\H.OH\\H.OH\\O''\\OH\end{array}\right.\right) + 2\left(\begin{array}{l}Ag\\Br\end{array}\right\}\Big)$$

Dibromo-pyrotartaric acid. Oxide of silver. Water. An unnamed acid.

Bromide of silver.



$$\left(C^6\left\{\begin{array}{l}C\left\{\begin{array}{l}OH\\O''\end{array}\right.\\Br\\Br\\H^2\\OH\end{array}\right.\right) + \left(\left.\begin{array}{l}Ag\\Ag\end{array}\right\}O\right) + \left(\left.\begin{array}{l}H\\H\end{array}\right\}O\right) = \left(C^6\left\{\begin{array}{l}C\left\{\begin{array}{l}OH\\O''\end{array}\right.\\OH\\OH\\H^2\\OH\end{array}\right.\right) + 2\left(\left.\begin{array}{l}Ag\\Br\end{array}\right\}\right)$$

Dibromo-salicylic acid. Oxide of silver. Water. Gallic acid.

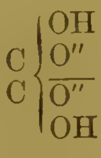
Bromide of silver.

The synthesis of tartaric acid was accomplished in 1860 by Kékulé on one hand, and by MM. Perkin and Duppa on the other: that of the homologue of tartaric acid by Kékulé in 1862, and that of gallic acid by MM. Kolbe and Lautemann in 1861.

In relation with the series of fatty acids, there is another series of which acrylic acid is the type, and of which the general formula is $C^nH^{2n-2}O^2$. Five of these acids are known, which as yet have not been obtained synthetically, viz., acrylic acid $C^3H^4O^2$, crotonic acid $C^4H^6O^2$, angelic acid $C^5H^8O^2$, pyroterebic acid $C^6H^{10}O^2$, and oleic acid $C^{18}H^{34}O^2$.

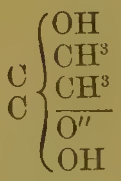
Dr. Frankland, in a work published in July 1865, has made known three new acids isomeric with crotonic, angelic, and pyroterebic acids; moreover, the properties of these acids have enabled him to determine the relations existing between these new compounds and their natural isomers on one hand, and the fatty acids on the other. These relations have taught Dr. Frankland a new synthetic process, by means of which he will probably achieve the synthesis of the natural acids of this series.

We have already seen how this chemist succeeded in substituting alcohol radicles for part of the oxygen which, in oxalic acid, is directly united to carbon, and how he thus obtained homologues of lactic acid: he has prepared dimethoxalic, etho-methoxalic, and diethoxalic acids in this manner:



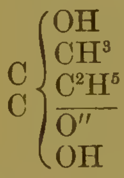
$$\begin{array}{l}C\\C\end{array}\left\{\begin{array}{l}OH\\O''\\\hline O''\\OH\end{array}\right.$$

Oxalic acid.



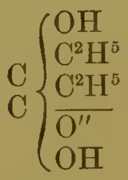
$$\begin{array}{l}C\\C\end{array}\left\{\begin{array}{l}OH\\CH^3\\CH^3\\\hline O''\\OH\end{array}\right.$$

Dimethoxalic acid.



$$\begin{array}{l}C\\C\end{array}\left\{\begin{array}{l}OH\\CH^3\\C^2H^5\\\hline O''\\OH\end{array}\right.$$

Etho-methoxalic acid.

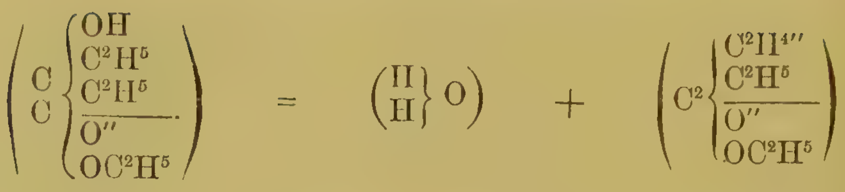


$$\begin{array}{l}C\\C\end{array}\left\{\begin{array}{l}OH\\C^2H^5\\C^2H^5\\\hline O''\\OH\end{array}\right.$$

Diethoxalic acid.

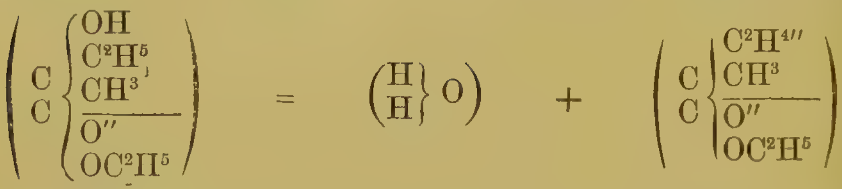
When submitted to the influence of terchloride of phosphorus or of phosphoric anhydride, the ethylic ethers of these three acids lose a molecule of water: this water is formed at the cost of one atom of hydroxyl contained in the acid employed, and of an atom of hydrogen taken from one of the alcohol radicles.

Thus we have:



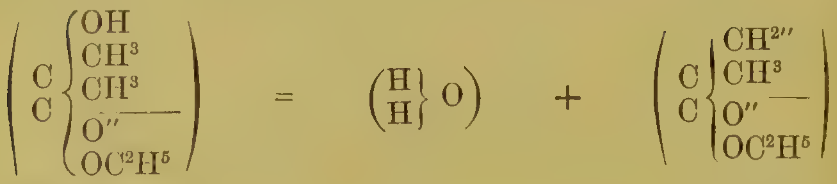
$$\left(\begin{array}{l}C\\C\end{array}\left\{\begin{array}{l}OH\\C^2H^5\\C^2H^5\\\hline O''\\OC^2H^5\end{array}\right.\right) = \left(\begin{array}{l}H\\H\end{array}\right\}O\Bigg) + \left(C^2\left\{\begin{array}{l}C^2H^{4''}\\C^2H^5\\\hline O''\\OC^2H^5\end{array}\right.\right)$$

Diethoxalate of ethyl. Water. Ethyl-crotonate of ethyl.



$$\left(\begin{array}{l}C\\C\end{array}\left\{\begin{array}{l}OH\\C^2H^5\\CH^3\\\hline O''\\OC^2H^5\end{array}\right.\right) = \left(\begin{array}{l}H\\H\end{array}\right\}O\Bigg) + \left(\begin{array}{l}C\\C\end{array}\left\{\begin{array}{l}C^2H^{4''}\\CH^3\\\hline O''\\OC^2H^5\end{array}\right.\right)$$

Etho-methoxalate of ethyl. Water. Methyl-crotonate of ethyl.



$$\left(\begin{array}{l}C\\C\end{array}\left\{\begin{array}{l}OH\\CH^3\\CH^3\\\hline O''\\OC^2H^5\end{array}\right.\right) = \left(\begin{array}{l}H\\H\end{array}\right\}O\Bigg) + \left(\begin{array}{l}C\\C\end{array}\left\{\begin{array}{l}CH^{2''}\\CH^3\\\hline O''\\OC^2H^5\end{array}\right.\right)$$

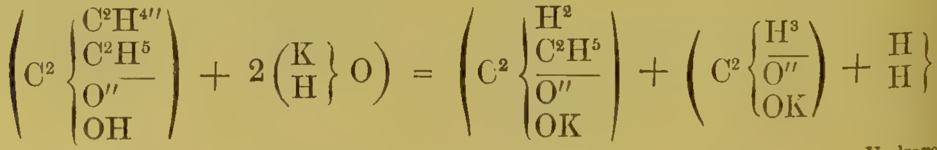
Dimethoxalate of ethyl. Water. Methacrylate of ethyl.

These different ethers may easily be saponified by an alcoholic solution of potash, and thus give rise to three acids which crystallize perfectly.

In the formation of these acids, it will be seen that the hexatomic group $C^2$ remains saturated. Although it loses OH, the radicles ethyl or methyl, which were monatomic, losing H become biatomic, and the equilibrium of the molecule is again established.

When one of these acids prepared by synthesis is heated with potash to 180° it splits up into two acids of the fatty series, disengaging hydrogen, in the same manner as the natural acids of which these acids are isomers. In this case ethyl-crotonic acid gives butyric and acetic acids; methyl-crotonic acid gives propionic and acetic acids; and metacrylic acid gives propionic and formic acids.

These reactions are easily explained on the supposition that the biatomic radicle contained in each of these acids is exchanged for $H^2$, giving one fatty acid, while this radicle unites with $O^2$ and forms the second. If two molecules of caustic potash be taken, the two atoms of oxygen contained in these two molecules unite with the biatomic radicle in question, and the two atoms of hydrogen of the potash are substituted for this radicle. We have thus the two fatty acids, which in presence of the potassium remaining from the potash form potassic salts and disengage $H^2$:

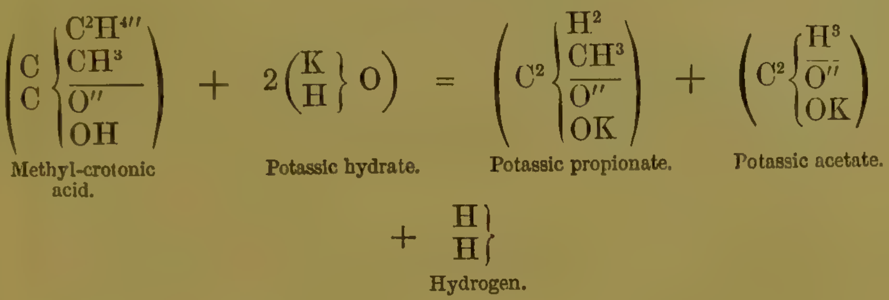


$$\left(C^2\left\{\begin{array}{l}C^2H^{4''}\\C^2H^5\\\hline O''\\OH\end{array}\right.\right) + 2\left(\begin{array}{l}K\\H\end{array}\right\}O\Bigg) = \left(C^2\left\{\begin{array}{l}H^2\\C^2H^5\\\hline O''\\OK\end{array}\right.\right) + \left(C^2\left\{\begin{array}{l}H^3\\\hline O''\\OK\end{array}\right.\right) + \left.\begin{array}{l}H\\H\end{array}\right\}$$

Ethyl-crotonic acid. Potassic hydrate. Potassic butyrate. Potassic acetate. Hydrogen.

It is true that, in cases in which the radicles found in the formula above and below the horizontal line contain different numbers of atoms of carbon, it might be admitted that the reaction results from the division of the molecule $C^2$ with which all these radicles are united. Thus the products which should theoretically be obtained are the same according to both hypotheses:

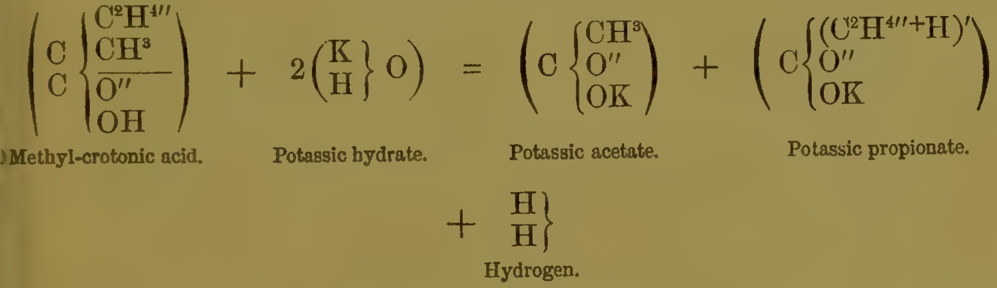
### FIRST HYPOTHESIS.



$$\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}C^2H^{4\prime\prime}\\CH^3\\\hline O^{\prime\prime}\\OH\end{array}\right.\right) + 2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right) = \left(C^2\left\{\begin{array}{l}H^2\\CH^3\\\hline O^{\prime\prime}\\OK\end{array}\right.\right) + \left(C^2\left\{\begin{array}{l}H^3\\\hline O^{\prime\prime}\\OK\end{array}\right.\right) + \left.\begin{matrix}H\\H\end{matrix}\right\}$$

Methyl-crotonic acid. Potassic hydrate. Potassic propionate. Potassic acetate. Hydrogen.

### SECOND HYPOTHESIS.

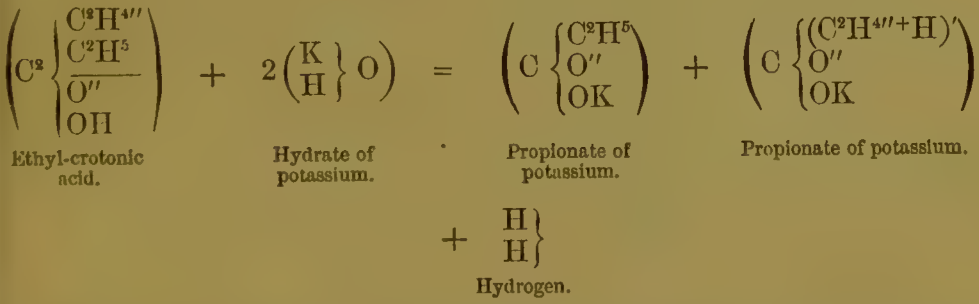


$$\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{array}{l}C^2H^{4\prime\prime}\\CH^3\\\hline O^{\prime\prime}\\OH\end{array}\right.\right) + 2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right) = \left(C\left\{\begin{array}{l}CH^3\\O^{\prime\prime}\\OK\end{array}\right.\right) + \left(C\left\{\begin{array}{l}(C^2H^{4\prime\prime}+H)^{\prime}\\O^{\prime\prime}\\OK\end{array}\right.\right) + \left.\begin{matrix}H\\H\end{matrix}\right\}$$

Methyl-crotonic acid. Potassic hydrate. Potassic acetate. Potassic propionate. Hydrogen.

Fortunately, these two hypotheses conduct to different conclusions in the case in which the two radicles placed above and below the horizontal line contain an equal amount of carbon, which causes the question to be decided in favour of the first hypothesis.

If ethyl-crotonic acid divided in conformity with the second hypothesis, instead of butyric and acetic acids it would furnish two molecules of propionic acid according to the subjoined reaction, which is not the case:

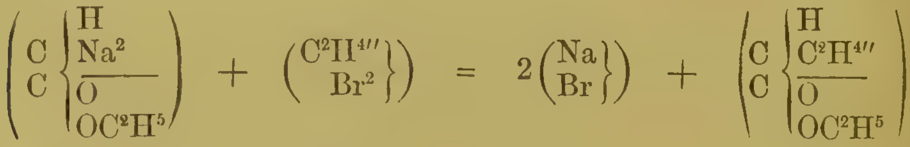


$$\left(C^2\left\{\begin{array}{l}C^2H^{4\prime\prime}\\C^2H^5\\\hline O^{\prime\prime}\\OH\end{array}\right.\right) + 2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O\right) = \left(C\left\{\begin{array}{l}C^2H^5\\O^{\prime\prime}\\OK\end{array}\right.\right) + \left(C\left\{\begin{array}{l}(C^2H^{4\prime\prime}+H)^{\prime}\\O^{\prime\prime}\\OK\end{array}\right.\right) + \left.\begin{matrix}H\\H\end{matrix}\right\}$$

Ethyl-crotonic acid. Hydrate of potassium. Propionate of potassium. Propionate of potassium. Hydrogen.

The mode according to which this reaction is accomplished being fixed, enabled Dr. Frankland to establish the rational formula of the natural acids isomeric with those he obtained synthetically, as already explained. This constitution once known, he perceived that there exists a very simple relation between the fatty acids and those of the acrylic series. These latter arising from the former by the substitution of a biatomic radicle for $H^2$, if the acid in the molecule of which the substitution takes place be acetic acid, the body produced is one of the natural acids of the acrylic series; if, on the contrary, it is a homologue of acetic acid, the body derived is one of the artificial acids of this series.

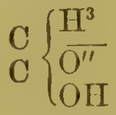
The substitution of a biatomic radicle for $H^2$ in the fatty acids has not yet been accomplished; but Dr. Frankland hopes to succeed with acetic acid by causing the bromide of ethylene or its homologues to act on disodacetic ether:



$$\left(\begin{array}{c}C\\C\end{array}\left\{\begin{array}{l}H\\Na^{2}\\\hline O\\OC^{2}H^{5}\end{array}\right.\right)+\left(\left.\begin{array}{r}C^{2}H^{4\prime\prime}\\Br^{2}\end{array}\right\}\right)=2\left(\left.\begin{array}{l}Na\\Br\end{array}\right\}\right)+\left(\begin{array}{c}C\\C\end{array}\left\{\begin{array}{l}H\\C^{2}H^{4\prime\prime}\\\hline O\\OC^{2}H^{5}\end{array}\right.\right)$$

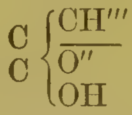
Disodacetate of ethyl. Bromide of ethylene. Bromide of sodium. Acrylate of ethyl.

The same chemist also thinks that another series of acids should exist, derived in a similar manner from acetic acid or its homologues, having this difference however, that instead of containing a biatomic radicle substituted for $H^2$, they would contain a triatomic radicle substituted for $H^3$:



$$\begin{array}{c}C\\C\end{array}\left\{\begin{array}{l}H^{3}\\\hline O^{\prime\prime}\\OH\end{array}\right.$$

Acetic acid.

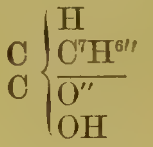


$$\begin{array}{c}C\\C\end{array}\left\{\begin{array}{l}CH^{\prime\prime\prime}\\\hline O^{\prime\prime}\\OH\end{array}\right.$$

Formylactic acid (hypothetical).

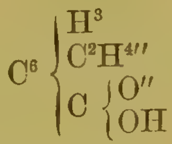
He furthermore supposes that, by processes analogous to those just described, a series of acids might be obtained which would bear the same relation to the aromatic acids that acrylic acid and its homologues bear to the fatty acids.

One acid of this nature, cinnamic acid, is already known, but it is difficult at present to say whether it should be considered as toluene-acetic acid or as ethylene-benzoic acid: it may be represented by either of the two following formulæ:



$$\begin{array}{c}C\\C\end{array}\left\{\begin{array}{l}H\\C^{7}H^{6\prime\prime}\\\hline O^{\prime\prime}\\OH\end{array}\right.$$

Toluene-acetic acid.



$$C^{6}\left\{\begin{array}{l}H^{3}\\C^{2}H^{4\prime\prime}\\C\left\{\begin{array}{l}O^{\prime\prime}\\OH\end{array}\right.\end{array}\right.$$

Ethylene-benzoic acid.

Cinnamic acid has been already obtained synthetically by two different processes; the first of which was discovered by Bertagnini in 1857, and consists in heating a mixture of chloride of acetyl and essential oil of bitter almonds in a closed vessel:

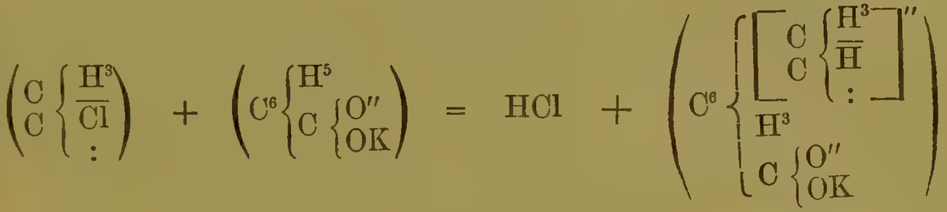
$$\underset{\text{Chloride of acetyl.}}{(C^2H^3OCl)} + \underset{\text{Benzoic aldehyd.}}{(C^7H^6O)} = \underset{\text{Cinnamic acid.}}{(C^9H^8O^2)} + \underset{\text{Hydrochloric acid.}}{HCl}$$

This reaction cannot be explained by our formulæ of constitution. It is probably accompanied by a complete change of state of the molecule.

The second process was also discovered in 1857 by M. Harnitz-Harnitzky. This chemist having caused the benzoate of barium to act on the chloracetene he had prepared by treating aldehyd with the oxychloride of carbon, obtained chloride of potassium and cinnamic acid.

This reaction probably takes place in two stages:

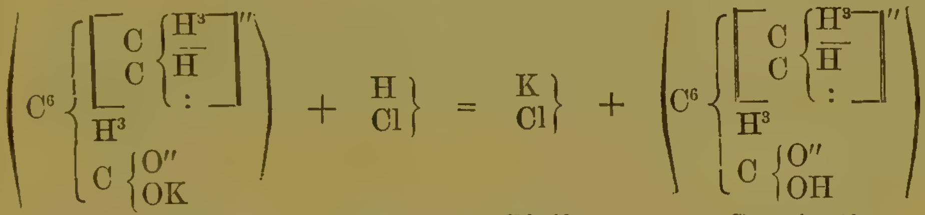
### FIRST STAGE.



$$\left(\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\\overline{Cl}\\:\end{matrix}\right.\right) + \left(C^6\left\{\begin{matrix}H^5\\C\left\{\begin{matrix}O''\\OK\end{matrix}\right.\end{matrix}\right.\right) = HCl + \left(C^6\left\{\begin{matrix}\left[\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\\overline{H}\\:\end{matrix}\right.\right]''\\H^3\\C\left\{\begin{matrix}O''\\OK\end{matrix}\right.\end{matrix}\right.\right)$$

Chloracetene. Benzoate of potassium. Hydrochloric acid. Cinnamate of potassium.

### SECOND STAGE.



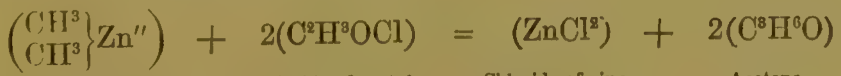
$$\left(C^6\left\{\begin{matrix}\left[\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\\overline{H}\\:\end{matrix}\right.\right]''\\H^3\\C\left\{\begin{matrix}O''\\OK\end{matrix}\right.\end{matrix}\right.\right) + \left.\begin{matrix}H\\Cl\end{matrix}\right\} = \left.\begin{matrix}K\\Cl\end{matrix}\right\} + \left(C^6\left\{\begin{matrix}\left[\begin{matrix}C\\C\end{matrix}\left\{\begin{matrix}H^3\\\overline{H}\\:\end{matrix}\right.\right]''\\H^3\\C\left\{\begin{matrix}O''\\OH\end{matrix}\right.\end{matrix}\right.\right)$$

Cinnamate of potassium. Hydrochloric acid. Chloride of potassium. Cinnamic acid.

These two syntheses are complete, as benzoic and acetic acids, and consequently their aldehyds have been prepared synthetically.

We have thus completed the history of the different methods which are general, or appear likely to become so, for effecting the synthesis of organic compounds: we will now speak in order of date of certain syntheses which as yet are not general.

In 1860 the acetones, which up to that time had only been prepared by the distillation of the calcic salts of monatomic acids, that is to say, by an analytical process, were prepared synthetically by Freund and Pebal, by causing zinc-ethyl or zinc-methyl to react on the chloride of acetyl or of any other acid radicle:



$$\underset{\text{Zinc-methyl.}}{\left(\left.\begin{matrix}CH^3\\CH^3\end{matrix}\right\}Zn''\right)} + \underset{\text{Chloride of acetyl.}}{2(C^2H^3OCl)} = \underset{\text{Chloride of zinc.}}{(ZnCl^2)} + \underset{\text{Acetone.}}{2(C^3H^6O)}$$

Recently, in 1865, Friedel accomplished the same synthesis by having recourse to the reaction of methylate of sodium on chloracetene:

$$\underset{\substack{\text{Methylate of}\\\text{sodium.}}}{\left(\left.\begin{matrix}CH^3\\Na\end{matrix}\right\}O\right)} + \underset{\text{Chloracetene.}}{(C^2H^3Cl)} = \underset{\text{Acetone.}}{(C^3H^6O)} + \underset{\substack{\text{Chloride}\\\text{of sodium.}}}{(NaCl)}$$

Later still, in 1866, M. Wanklyn also prepared acetone synthetically: his process consists in causing oxide of carbon to act on sodium-methyl. Carbonyl CO'' is substituted for the sodium, which becomes free:

$$\underset{\text{Sodium-methyl.}}{2(CH^3Na)} + \underset{\substack{\text{Oxide of}\\\text{carbon.}}}{CO} = \underset{\text{Acetone.}}{\left((CO)''\left\{\begin{matrix}CH^3\\CH^3\end{matrix}\right.\right)} + \underset{\text{Sodium.}}{\left.\begin{matrix}Na\\Na\end{matrix}\right\}}$$

In 1861, Boutlerow obtained by synthesis a substance which appeared to him to be analogous to the sugars. This substance is produced along with formic acid, when dioxy-methylene is heated with lime. M. Boutlerow thinks that its formula is $C^7H^{14}O^6$, though its analysis does not support this view. However, according to this hypothesis, the reaction is easily explained. We have:

$$\underset{\text{Dioxy-methylene.}}{4(C^2H^4O^2)} = (C^7H^{14}O^6) + \underset{\text{Formic acid.}}{(CH^2O^2)}$$

This new substance has received the name of methylenitane, indicating its origin and its analogy with mannitane.

In the course of the same year, 1861, Kolbe obtained formic acid by transmitting a mixture of carbonic anhydride and sodium over heated potassium:

$$\underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{2(CO^2)} + \underset{\text{Water.}}{(H^2O)} + \underset{\text{Potassium.}}{K^2} = \underset{\substack{\text{Potassic}\\\text{formiate.}}}{(CHKO^2)} + \underset{\substack{\text{Potassic}\\\text{bicarbonate.}}}{\left(\left.\begin{matrix}CO''\\H\\K\end{matrix}\right\}O^2\right)}$$

During the same year also, MM. Lieben and Baüer succeeded in preparing several bodies whose molecules are more complex than those of their generators.

These chemists having caused chlorine to act on ether, substituted two atoms of chlorine for two atoms of hydrogen, and gave the compound they obtained the name of monochlorinated ether*. This latter, on reacting with zinc-ethyl, exchanges an atom of its chlorine for ethyl, and gives a compound having for formula $\left(\left.\begin{matrix}C^2H^4(C^2H^5)\\C^2H^4Cl\end{matrix}\right\}O\right)$:

---

* Mono- and not bi-chlorinated, because M. Malaguti had applied the name bichlorinated to that ether in which four atoms of chlorine are substituted for four of hydrogen, the formula of ether not having as yet been doubled.

$$2\left(\left.\begin{matrix}C^2H^4Cl\\C^2H^4Cl\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}Zn''\right) = \left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}Zn''\right) = 2\left(\left.\begin{matrix}C^2H^4(C^2H^5)\\C^2H^4Cl\end{matrix}\right\}O\right)$$

Monochlorinated ether. Zinc-ethyl. Chloride of zinc. Chlor-ethylic ether.

Chloro-ethylic ether, heated in a sealed tube with a fresh quantity of zinc-ethyl, exchanges its atom of chlorine for ethyl, and furnishes diethylic ether:

$$2\left(\left.\begin{matrix}C^2H^4(C^2H^5)\\C^2H^4Cl\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}Zn''\right) = \left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}Zn''\right) + 2\left(\left.\begin{matrix}C^2H^4(C^2H^5)\\C^2H^4(C^2H^5)\end{matrix}\right\}O\right)$$

Chlor-ethylic ether. Zinc-ethyl. Chloride of zinc. Dioxethylic ether.

Later, in 1864, M. Lieben, continuing the study of monochlorinated ether, succeeded in substituting oxethyl or oxymethyl for one or for two atoms of chlorine. (The dioxymethylic product has not yet been obtained):

$$\left(\left.\begin{matrix}C^2H^4Cl\\C^2H^4Cl\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}CH^3\\Na\end{matrix}\right\}O\right) = \left(\left.\begin{matrix}Na\\Cl\end{matrix}\right\}\right) + \left(\left.\begin{matrix}C^2H^4(CH^3O)\\C^2H^4Cl\end{matrix}\right\}O\right)$$

Monochlorinated ether. Methylate of sodium. Chloride of sodium. Chloroxymethylic ether.

$$\left(\left.\begin{matrix}C^2H^4Cl\\C^2H^4Cl\end{matrix}\right\}O\right) + 2\left(\left.\begin{matrix}C^2H^5\\Na\end{matrix}\right\}O\right) = 2\left(\left.\begin{matrix}Na\\Cl\end{matrix}\right\}\right) + \left(\left.\begin{matrix}C^2H^4(C^2H^5O)\\C^2H^4(C^2H^5O)\end{matrix}\right\}O\right)$$

Monochlorinated ether. Ethylate of sodium. Chloride of sodium. Dioxethylic ether.

Quite recently, Lieben has published in the German journals an epitome of an important work, wherein he proves that the preceding formulæ should be modified, the chlorine, ethyl and methyl being substituted, not for one atom of hydrogen in each molecule of ethyl, but for two atoms of hydrogen in the same molecule of ethyl. On submitting the chloro-ethylic compound to the action of concentrated hydriodic acid, Lieben obtained iodide of butyl, iodide of ethyl, and iodine. This reaction takes places in two stages:

### FIRST STAGE.

$$\left(\left.\begin{matrix}C^2H^3.Cl.C^2H^5\\C^2H^5\end{matrix}\right\}O\right) + 2\left(\left.\begin{matrix}H\\I\end{matrix}\right\}\right) = \left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right) + \left(\left.\begin{matrix}[C^2H^3.Cl.C^2H^5]\\I\end{matrix}\right\}\right)$$

Chlor-ethylic ether. Hydriodic acid. Water. Chlorinated iodide of butyl.

$$+ \ (C^2H^5I)$$

Iodide of ethyl.

### SECOND STAGE.

$$\left(\left.\begin{matrix}[C^2H^3.Cl.C^2H^5]\\I\end{matrix}\right\}\right) + 2\left(\left.\begin{matrix}H\\I\end{matrix}\right\}\right) = \left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right) + \left.\begin{matrix}I\\I\end{matrix}\right\}$$

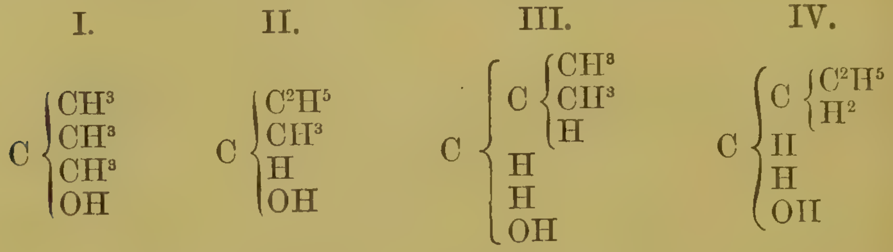
Chlorinated iodide of butyl. Hydriodic acid. Hydrochloric acid. Iodine.

$$+ \left(\left.\begin{matrix}[C^2H^4.C^2H^5]\\I\end{matrix}\right\}\right)$$

Iodide of butyl

SCHOOL OF MEDICINE

Lieben asks what is the constitution of the butyric alcohol corresponding to this iodide of butyl. In order to solve this problem he first seeks how many isomeric butylic alcohols can exist, and finds that there may be four, having the following rational formulæ:



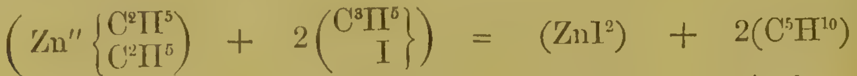
I. $C\left\{\begin{matrix}CH^3\\CH^3\\CH^3\\OH\end{matrix}\right.$ II. $C\left\{\begin{matrix}C^2H^5\\CH^3\\H\\OH\end{matrix}\right.$ III. $C\left\{\begin{matrix}C\left\{\begin{matrix}CH^3\\CH^3\\H\end{matrix}\right.\\H\\H\\OH\end{matrix}\right.$ IV. $C\left\{\begin{matrix}C\left\{\begin{matrix}C^2H^5\\H^2\end{matrix}\right.\\H\\H\\OH\end{matrix}\right.$

He then establishes that the formulæ I. and III. cannot represent the constitution of the alcohol in question, because it necessarily contains in its molecule the ethyl which was introduced synthetically, and that these formulæ correspond to bodies which would not contain this radicle.

There therefore remain the formulæ II. and IV.

The formula IV. is that of the butyric alcohol of fermentation; M. Lieben's alcohol being different from the latter, and appearing rather to resemble the butylic pseudo-alcohol of M. de Luynes. The 2nd formula therefore is that which represents its constitution.

In 1862, Wurtz accomplished the synthesis of amylene by causing iodide of allyl to act on zinc-ethyl:

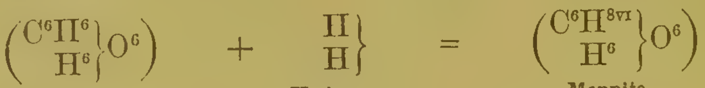


$$\left(Zn''\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right.\right) + 2\left(\begin{matrix}C^3H^5\\I\end{matrix}\right\}\Bigg) = (ZnI^2) + 2(C^5H^{10})$$

Zinc-ethyl. Iodide of allyl. Iodide of zinc. Amylene.

Later still, he showed that the same results are obtained on substituting a mixture of sodium and iodide of ethyl for the zinc-ethyl.

In the course of 1862 Linnemann succeeded in combining nascent hydrogen with glucose, which it converts into mannite:



$$\left(\begin{matrix}C^6H^6\\H^6\end{matrix}\right\}O^6\Bigg) + \left.\begin{matrix}H\\H\end{matrix}\right\} = \left(\begin{matrix}C^6H^{8\,vi}\\H^6\end{matrix}\right\}O^6\Bigg)$$

Glucose. Hydrogen. Mannite.

In 1861, Lœvig, on causing nascent hydrogen to act on oxalate of ethyl, obtained a new acid, which he called desoxalic acid, a fermentable sugar being formed at the same time; in 1862 he succeeded in decomposing desoxalic acid into carbonic anhydride and paratartaric acid, by heating it with dilute sulphuric acid, which appears to exercise simply a catalytic action:

$$(C^5H^6O^8) = CO^2 + (C^4H^6O^6)$$

Desoxalic acid. Carbonic anhydride. Paratartaric acid.

Towards the close of 1862, Mendius transformed the cyanides of alcohol radicles into amines of a series higher by one term than their own. To effect this, he fixed four molecules of hydrogen on the cyanides by placing them in presence of a mixture of zinc and sulphuric acid:

$$\underset{\text{Cyanide of methyl.}}{\left(\left.\begin{matrix}CN\\CH^3\end{matrix}\right\}\right)} + \underset{\text{Hydrogen.}}{2\left(\left.\begin{matrix}H\\H\end{matrix}\right\}\right)} = \underset{\text{Ethylamine.}}{\left(\left.\begin{matrix}C^2H^5\\H\\H\end{matrix}\right\}N\right)}$$

In 1863, Boutlerow obtained an isomer of butylic alcohol by causing water to act on the product of the reaction of oxychloride of carbon with zinc-methyl. The same body is also formed when chloride of acetyl is substituted for oxychloride of carbon. It must therefore be admitted that, in the first of these reactions, an atom of methyl is substituted for an atom of chlorine, thereby transforming the oxychloride of carbon into chloride of acetyl, and that, afterwards, a second molecule of zinc-methyl entering into reaction, two atoms of methyl are substituted for an atom of oxygen. The result of this latter action is a chlorinated body which, on contact with water, exchanges its chlorine for hydroxyl and furnishes the isomer of butylic alcohol of which we speak:

$$\underset{\text{Oxychloride of carbon.}}{2\left(C\left\{\begin{matrix}O''\\Cl\\Cl\end{matrix}\right.\right)} + \underset{\text{Zinc-methyl.}}{\left(\left.\begin{matrix}CH^3\\CH^3\end{matrix}\right\}Zn''\right)} = \underset{\text{Chloride of zinc.}}{\left(\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}Zn''\right)} + \underset{\text{Chloride of acetyl.}}{2\left(C\left\{\begin{matrix}O''\\CH^3\\Cl\end{matrix}\right.\right)}$$

$$\underset{\text{Chloride of acetyl.}}{\left(C\left\{\begin{matrix}O''\\CH^3\\Cl\end{matrix}\right.\right)} + \underset{\text{Zinc-methyl.}}{\left(\left.\begin{matrix}CH^3\\CH^3\end{matrix}\right\}Zn''\right)} = \underset{\text{Oxide of zinc.}}{ZnO} + \underset{\text{Trimethylated chloride of methyl.}}{\left(C\left\{\begin{matrix}CH^3\\CH^3\\CH^3\\Cl\end{matrix}\right.\right)}$$

$$\underset{\text{Trimethylated chloride of methyl.}}{\left(C\left\{\begin{matrix}CH^3\\CH^3\\CH^3\\Cl\end{matrix}\right.\right)} + \underset{\text{Water.}}{\left(\left.\begin{matrix}H\\H\end{matrix}\right\}O\right)} = \underset{\text{Hydrochloric acid.}}{\left(\left.\begin{matrix}H\\Cl\end{matrix}\right\}\right)} + \underset{\text{Trimethylated methylic alcohol (trimethyl-carbinol).}}{\left(C\left\{\begin{matrix}CH^3\\CH^3\\CH^3\\OH\end{matrix}\right.\right)}$$

In 1864, by causing sodium to act on monobromacetic acid, M. Baeyer produced an acid which is three times more complex than acetic acid, and gave it the name of aceconitic acid. In this reaction the sodium seizes the bromine and the three residues unite, losing an atom of hydrogen:

$$\underset{\text{Bromacetic acid.}}{6(C^2H^3BrO^2)} + \underset{\text{Sodium.}}{3\left(\left.\begin{matrix}Na\\Na\end{matrix}\right\}\right)} = \underset{\text{Sodic bromide.}}{6\left(\left.\begin{matrix}Na\\Br\end{matrix}\right\}\right)} + \underset{\text{Aceconitic acid.}}{2(C^6H^8O^6)} + \underset{\text{Hydrogen.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}}$$

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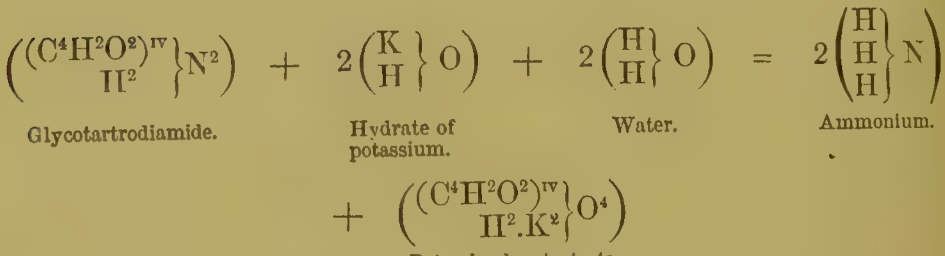
However, M. Baeyer, instead of using bromacetic acid, finds it preferable to substitute for it the bromacetate of ethyl; he therefore obtains, instead of free aceconitic acid, triethylic aceconitate, which furnishes the acid when saponified.

In 1865, M. Schögen produced synthetically an isomer of tartaric acid, different from all the modifications of this acid previously known. To effect this result, he combined two molecules of hydrocyanic acid with a molecule of glyoxal, and boiled the compound formed with potash. Ammonia was disengaged, and there was produced an alkaline salt of the new acid, called by M. Schögen glycotartaric acid:

$$(C^2H^2O^2) + 2(CNH) = \left(\left.\begin{matrix}(C^4H^2O^2)^{\text{iv}}\\ H^2\end{matrix}\right\}N^2\right)$$

Glyoxal. Hydrocyanic acid. Glycotartrodiamide.



$$\left(\left.\begin{matrix}(C^4H^2O^2)^{\text{iv}}\\ H^2\end{matrix}\right\}N^2\right) + 2\left(\left.\begin{matrix}K\\ H\end{matrix}\right\}O\right) + 2\left(\left.\begin{matrix}H\\ H\end{matrix}\right\}O\right) = 2\left(\left.\begin{matrix}H\\ H\\ H\end{matrix}\right\}N\right)$$

Glycotartrodiamide. Hydrate of potassium. Water. Ammonium.

$$+ \left(\left.\begin{matrix}(C^4H^2O^2)^{\text{iv}}\\ H^2.K^2\end{matrix}\right\}O^4\right)$$

Potassic glycotartrate.

Finally, during the past year M. Berthelot has obtained oxalic, malonic, and pyrotartaric acids by the oxidation of acetylene or ethylene and their homologues. (*See* pages 393–4).

We have thus given a summary of the progress made in organic synthesis during the last twenty-five years. In this we have not mentioned the alkaloids, because their syntheses are among those which we excluded at the commencement.

The synthetic results already obtained and those we have reason to anticipate show that all organic compounds may be prepared in the laboratory by means of the elements, and consequently the last barriers which appeared to exist between mineral and organic chemistry are removed.

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